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1995

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TEXTILE. PIELĂRIE

ON THE POROSITY OF MELANA FIBERS. METHODS OF QUANTITATIVE AND QUALITATIVE ESTIMATION

BY
OTILIA MÂLCOMETE and V. BLAŞCU

1. Introduction. In processes of fiber spinning from concentrated solutions of polymers, the number, shape and dimensions of the micro- and macrodefects in the fiber structure depend on a series of factors, such as: thermodynamic properties of the solution–polymer system and composition of the spinning bath, temperature, subsequent processing (e.g., washing, drying, drawing, thermofixation, a.s.o.) [1], [2].

The porous structure of fiber is also determined by the modality chosen for achieving the structural-fibrillar system, by association of the macromolecular chains [3],...,[5].

Thermal and wet-thermal treatments to which acrylic fibers are subjected after spinning may modify to a lesser or higher extent the porous structure, either through the pores opening or closing, or through their new distribution and reorientation.

For a thorough investigation of fibers porous structure a series of methods has been established, such as: mercury penetrometry [1], measurement of gas, vapours or solvents absorption [5],...,[7], or techniques such as densimetry, calorimetry [1] or electronic microscopy [6], [8].

2. Experimental. On considering the difficult techniques actually applied for the determination of fibers porosity, necessitating complex installations, we have employed densimetry and electronic microscopy [9].

Porosity has been detemined on Melana fibers as wrinkled cable, both nonfixed and fixed, produced in four operation lines.

Total porosity has been calculated with the following relation:

$$P = \frac{\rho_r - \rho_g}{\rho_r} \times 100, \ [\%],$$

where: ρ_r is real density of the fiber (without pores); ρ_g – geometrical density (pores included).

Real density has been determined by two methods, namely: the method of density gradient column on employing water–calcium nitrate solutions of various densities and the picnometric method, employed carbon tetrachloride as wetting liquid.

Density has been determined at constant temperature (20°C).

The calculation of density by the density gradient column made use of the relation:

$$\rho_r = \frac{(h - h_1)(\rho_2 - \rho_1)}{h_2 - h_1} + \rho_1, \ [\text{g/cm}^3],$$

where: ρ_r is sample density (real); ρ_1 and ρ_2 – densities of the liquids between which the sample is placed; h_1 and h_2 – heights of the two reference floating bodies; h – height of the sample on the column.

The picnometric method calculated density with the following relation:

$$\rho_r = \frac{M_{fb}\rho_1}{M_{fb} + M_1 + M_2}, \ [\text{g/cm}^3]$$

where: M_{fb} is weight of fibers in air; M_1 – weight of the picnometer with liquid; M_2 – weight of the picnometer with liquid and with the introduced fibers; ρ_1 – liquid density (ρ_{CCl_4}=1.593 g/cm^3).

Geometrical (apparent) density has been determined in two variants for the establishment of the fiber total volume, namely: measurement of fiber thickness (on a lanameter, at a magnification of 500×) for fiber segments of constant weight and measurement of the cross section surface (obtained by introducing the fibers in collodium and parrafin, crossing being performed at 20-25 μm).

The section surface has been obtained by plotting the microscopic image, followed by its planimetering.

Under such circumstances, the geometric volume has been calculated with the following relations:

$$V_g = \bar{d}^2 \cdot l \cdot n \quad \text{or} \quad V_g = \bar{A} \cdot l \cdot n, \ [\text{mm}^3],$$

where: $\bar{d}$ and $\bar{A}$ represent the average diameter and average surface, respectively; n – number of fibers in the segment; l – fiber length.

Density has been calculated with the relation:

$$\rho_{\text{geom.}} = \frac{m_{fb}}{V_g}, \ [\text{g/cm}^3],$$

where m_{fb} is weight of the fiber segment.

The experimental values are listed in Table 1.

Table 1

Fibers Densities

Fiber	Applied treatment	Real density, [g/cm^3]		Geom. density, [g/cm^3]		$\rho_{col.} - \rho_{picn.}$
		Column	Picnometer	Diameter	Surface	
Melana II	Nonfixed(N)	1.1700	1.1543	1.139	1.130	0.0157
	Fixed (F)	1.1789	1.1650	1.159	1.151	0.0139
Melana III	N	1.1780	1.1590	1.151	1.148	0.0190
	F	1.1820	1.1667	1.163	1.166	0.0153
Melana IV	N	1.1785	1.1608	1.148	1.139	0.0176
	F	1.1815	1.1675	1.155	1.148	0.0140
Melana V	N	1.1650	1.1481	1.134	1.125	0.0169
	F	1.1785	1.1640	1.152	1.144	0.0145

On analyzing the values of real density, determined by the column and picnometric method, significant differences are to be observed, regardless of the process line utilized for the fabrication of fibers, as well as of their fixed or non-fixed state. Differences in density may be explained by the fact that the liquids employed do not penetrate equally the fibers cavities and micropores. Thus, when applying the density column method, the solution penetration is more intense, thus replacing the air from microcavities, on having in view, too, that the duration according to which density has been determined was of 24 h. With the picnometric method, measurements have been made immediately after immersion. Concomitantly with this, the molecules of carbon tetrachloride do not penetrate the fiber "closed" regions, non-penetrated macrovacuoles thus remaining [10].

Porosity has been calculated under experimental conditions established with the following relations:

- total porosity: $P_t = \frac{\rho_{col.} - \rho_{geom.}}{\rho_{col.}} \cdot 100$, [%];
- closed porosity: $P_c = \frac{\rho_{col.} - \rho_{picn.}}{\rho_{col.}} \cdot 100$, [%];
- open porosity: $P_o = P_t - P_c$, [%].

The average values, given in Table 2, evidence that the total porosity is higher with non-fixed than with fixed fibers. Fixation induces lowering of total porosity and maintaining of close and open porosities. If, in the case of Melana II and III fibers, more pronounced differences exist between fixed and non-fixed fibers, with Melana IV and V, the differences recorded as to total porosity are lower, which indicates that fixation has not been performed correspondingly.

Table 2
Fibers Porosities

Fiber	Applied treatment	Porosity, [%]		
		Total	Internal	Open
Melana II	N	2.65	1.34	1.31
	F	1.69	1.17	0.52
Melana III	N	2.30	1.62	0.68
	F	1.60	1.29	0.31
Melana IV	N	2.58	1.49	1.09
	F	2.24	1.18	1.06
Melana V	N	2.66	1.45	1.21
	F	2.25	1.23	1.02

Measurement of porosity has been also made through scavenging electronic microscopy, on cross sections of the fibers obtained on line III, previously treated thermally at various temperatures, in order to follow the variation of porosity versus temperature.

Porosity has been determined by planimetry starting from the electromicrographic images (magnified 10,000×) of the pores and fissures, as compared with the section surface.

The porous structure of the thermally treated fibers has been correlated with

Table 3

Data on Melana III Fibers

Temperature °C	$\frac{A_{breaks} \cdot 100}{A_{total}}$	I_c %	$\Delta n \cdot 10^{-3}$	$C_{residual}$ on boiling,[%]
Nonfixed	3.09	43.97	−3.54	13.45
80	2.26	44.61	−4.36	12.37
100	5.33	46.04	−5.47	11.00
120	8.30	48.03	−5.57	10.48
140	10.65	49.38	−5.72	5.44

other structural characteristics, such as: crystallinity index, optical birefrigerence and residual contraction on boiling.

Analysis of these values, listed in Table 3, leads to the following conclusions:

– a slight reduction of the pores is to be observed at a temperature of 80°C, which means, too, an increase of crystallinity and orientation;

– at higher temperatures, porosity increase, concomitantly with increasing crystallinity and orientation;

– the residual contraction obtained by boiling decreases with increasing temperature.

Fig. 1

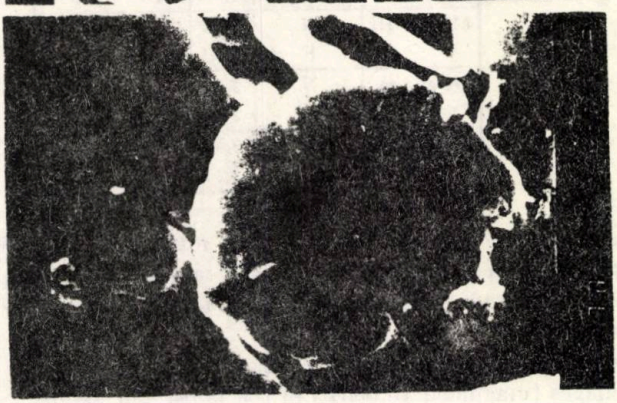

Fig. 2

On following the images offered by electronic microscopy, too, the observation to be made is that at a temperature of 100°C, some pronounced breaks do appear, while at 120 and 140°C, the existent microcavities become more ample, concomitantly with increasing breaks (Figs. 1,...,5).

Fig. 3

Fig. 4

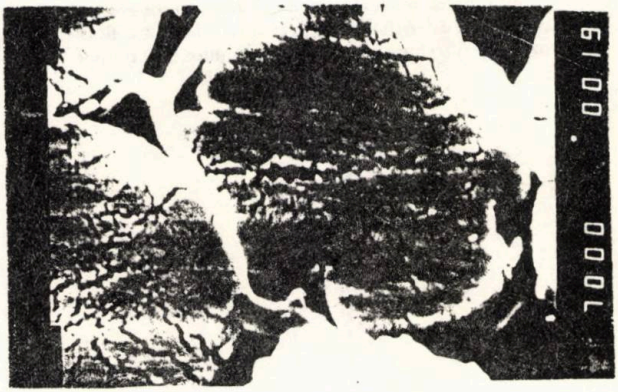

Fig. 5

A comparative analysis of these data evidences no correlation between the apparition and development of the porous structure, and crystallinity and orientation.

3. Conclusion. The conclusion to be drawn is that Melana-type fibers possess a complex porosity, that may influence differentially the accessibility of the solutions of dyes, with certain consequences in the uniformity of dyeing. At the same time, the porous structure becomes more pronounced after thermal treatments, accompanied by the apparition and development of significant breaks.

All these conclusive observations might be useful in analysis on the fabrication of fibers, for a better correlation of all factors influencing the fiber structure.

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POROZITATEA FIBRELOR MELANA. METODE DE APRECIERE CANTITATIVĂ ŞI CALITATIVĂ

(Rezumat)

Se propune o nouă metodă de apreciere cantitativă a porozităţii fibrelor textile, în particular a fibrelor Melana, folosind tehnici densimetrice combinate cu microscopia electronică.

Sunt analizate influenţele diferiţilor factori asupra porozităţii fibrelor Melana.

Se compară porozitatea fibrelor obţinute pe mai multe linii tehnologice.

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LE COMPORTEMENT À LA FATIGUE ET RUPTURE DES FIBRES ET DES FILS DE TYPE P.V.A.

PAR
YO VERSCHUREN et IRINA TĂRĂBOANŢĂ

1. Introduction. Dans le domaine textile, on dit qu'un matériel „fatigue" quand après une période d'utilisation (en peu de temps ou en beaucoup de temps) il est déformé de façon irréversible, avec la présentation de zones de destruction.

La fatigue est un processus évolutif du mécanisme de diminution graduelle des caractéristiques mécaniques, en comparaison avec l'état initial.

Le mécanisme de la rupture des fibres textiles a été expliqué par A. P e t e r l i n sur le principe du modèle microfibrilaire avec cathènes pliés qui correspond le mieux, par exemple microfibriles ou fibriles, jouent un rôle important dans le phénomène de la rupture.

On sait que les produits macromoleculaires sous l'action des forces rapides, concentrés sur des petites surfaces, à côté des phénomènes de coule sont aussi les processus de destruction accompagnes de la scission de quelques liaisons chimiques. Jamais ces processus ne se développent sur toute la section et en même temps mais se propagent avec différentes vitesse par passages succesifs.

L'apparition des tensions inégales sur la zone de rupture du matériel sollicité, en général, conduit aux effets complexes caractérisés par les aspets suivants: la modification de la position réciproque des cathènes macromoleculaires dans le matériel sollicité; la formation de nouvelles surfaces correspondants pour une certaine énergie superficielle accompagné de la scission des nombreuse valences secondaires et parfois principales; la transformation d'une fraction de l'énergie élastique en scission dans une onde qui se propage à la vitesse du son, creant la propagation du processus de scission et l'apparition de la destruction visqueuse accompagnée du phénomène d'écoulement dans les domaines amorphes et la scission dans les domaines cristallins.

Les phénomenènes de destruction mécanique sont conditionnés par la vitesse de la sollicitation, durée et température. Les sollicitations répetées finissent aussi par la destruction. Dans le processus de vieillissement, apparaît la scission des liaisons chimique avec la formation de macroradicaux libres, qui peuvent déterminer ultérieurement des processus de destruction. Dans le prôcessus de la fatique le nombre des macroradicaux libres formés est petit pour chaque cycle de sollicitation. Par l'accroissement du régime mécanique augmente aussi le nombre de macromolecules scindés – donc l'apparition d'un grand nombre de macroradicaux.

Puisque dans le processus de fatigue, les fibres souffrent toujours de deformations hétérogènes dans différents microcavités, vont apparaître des quantités différents de macroradicaux. Les réactions chimiques se manifesteront en priorité là où la concentration des macroradicaux sera plus grande. Ainsi, nous obtiendrons des structures modifiées uniquement dans des microcavités isolés, où se produira la destruction primaire du matériel et en conséquence, l'apparition des microfissure qui progressent et se propageant rapidement, affectuant la fibre dans beaucoup plus de zones et à la fin la rupture.

Donc, la fatigue des fibres se réalise par chemin „mécanochimique", parce que les actions mécaniques initient, accélérent ou freinent différents processus chimiques qui conduisent dans la dernière instance à la destruction.

Une interprétation juste du phénomène de fatigue des fibres créée les prémisses des destruction sous l'action statique prolongée, ou par multiples deformations. Donc, il est nécessaire de créer un régime mécanique modéré pour réduire au minimum le nombre des radicaux libres.

2. Partie expérimentale. Dans cet article, on a poursuivi le comportement à la fatigue et rupture du fil filamentaire de type p.v.a. soluble dans l'eau qui est utilisé beaucoup comme support pour les fibres en laine, coton à le but de la réalisation des tissus à poids appréciablement réduit (après lavage) destinés à des articles de luxe.

Du point de vue des caractéristiques de structure, le fil filamentaire de type p.v.a. soluble n'a pas une structure réticulée comme dans le cas des fibres des type p.v.a. Kuralon insoluble dans l'eau. On peut observer cette différence dans les photo effectuées à l'aide du microscope optique Nikon (Figs.1 *a*, *b*, 2 *a*, *b*).

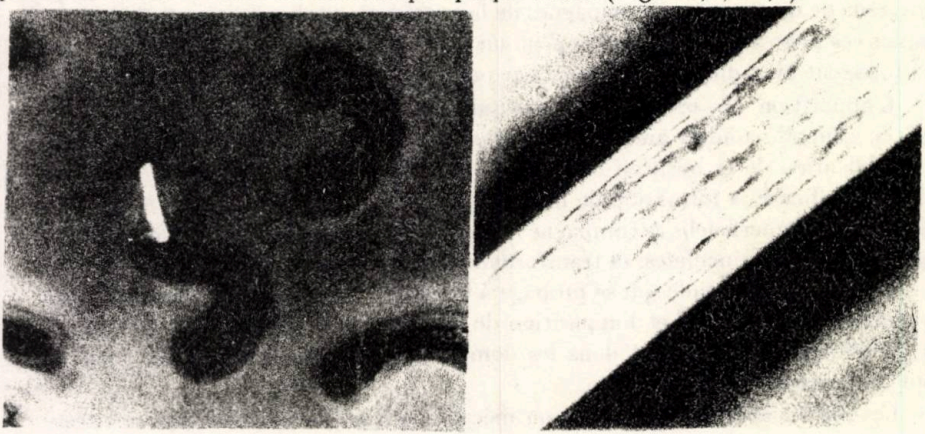

Fig. 1.– Fibres p.v.a. Kuralon-insoluble dans l'eau, obtenu par filage humide et coagulation dans bain de Na_2SO_4: *a* – la section transversale; *b* – la distinction de la surface extérieure de la fibre.

Dans la Fig.1 *a* on observe que les fibres de type p.v.a. insoluble, obtenues par filage humide – sectioné transversal, présente deux formes de structure: à l'extérieur

Fig. 2.– Le fil filamentaire de type p.v.a. Solvron SX-soluble dans l'eau, obtenu par filage sec: *a* – la section transversale; *b* – l'image longitudinale (dessus le fil de type p.v.a.).

le manteau qui est luisant et transparent et à l'intérieur le coeur qui est creusé et spongieux.

Dans la Fig.2 *a* pour le fil filamentaire de type p.v.a. Solvron SX, soluble dans l'eau on peut observer un autre aspect de la section transversale – sans le coeur spongieux.

Cette différence de structure entre ces deux photos est dûe au fait que dans le premier cas les fibres sont insolubilisés completement par bloquage partiel des hydroxyles p.v.a. par leur réaction avec une aldéhyde.

On croit que la surface extérieure (le manteau) est formée de la coagulation et étiration de la surface dans l'état de coule du filament liquide relatif après extrusion. Cependant l'intérieur poreux est formé à cause du retard de la coagulation et déshydration causé de la surface extérieure formée antérieure [1].

La forme et la structure de la section affectent les proprietés de la fibre, spécialement le comportement à la teinture des fibres Kuralon.

Beaucoup d'études publiées ont rapporté des méthodes et conditions de production des fibres à section uniforme circulaire [1]. En général, la circulairité de la section des fibres augmente si la concentration de la solution de filage augmente [2], quand la concentration du bain de coagulation baisse [3] ou quand la température du bain de coagulation est augmentée [4].

L'addition augmentée des réactifs chimiques comme H_2SO_4 [2] NaOH [2], NaCl [3], Na_2SO_4 [3], ou glicérine [3] conduit à l'augmentation de la circulairité.

On sait que l'uniformité de la section transversale de la fibre est proportionnellement, croissante à l'utilisation des bains de coagulation, avec concentration basse [4] ou l'utilisation d'une vitesse de filage plus lente [5].

Les méthodes décrites de croissante de la circulairité ou d'uniformité de la section de la fibre fait la completation que doit prévenir la coagulation rapide de la zone de la surface du filamente liquide et prévenement la différence de coagulation entre la zone de surface et l'intérieur des filaments liquides [1].

Dans beaucoup de cas, ces conditions ne sont pas suffisamment attractives pour être appliquées en pratique à l'obtention des fibres p.v.a.

Les analyses de microscopie électronique effectuées ont mis en évidence les phénomènes de la fatigue et rupture après sollicitation dans le cas des fibres p.v.a. insoluble dans l'eau (Kuralon) et du fil filamentaire de type p.v.a. soluble dans l'eau (Solvron SX).

Pour l'investigation du phénomène de la fatigue et rupture après sollicitations, un microscope électronique SEM 505-Philips a été utilisé. La rupture de la fibre est déterminée par la propagation rapide des microfissures apparues après la destruction primaire dans la structure des microcavités isolées.

Pour la distinction de la rupture d'une seule fibre de type p.v.a. insoluble dans l'eau le dynamomètre Fafegraph a été utilisé afin d'obtenir des courbes effort–alongement. La fibre dans Fig.3 a été introduite dans l'air liquide.

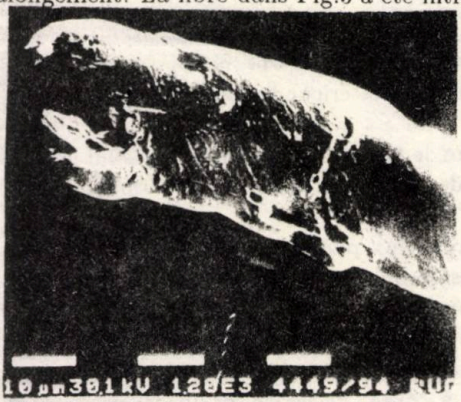

Fig. 3.– La rupture dans l'air liquide d'une fibre de type p.v.a. Kuralon.

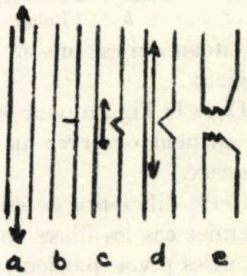

Fig. 4.– La présentation des phénomènes qui se produisent dans la fibre, jusqu'à la rupture de la fibre.

Dans le voisinage de la rupture on peut observer un grand nombre de fissures qui sont initiations dans la rupture.

Les phénomènes qui se produisent dans la fibre [6] jusqu'à la rupture de la fibre sont présentés en Fig.4, où *a* est la fibre avant de sollicitation; *b* – l'apparition de la fissure; *c* – l'ouverture immédiate; *d* – l'augmentation de l'ouverture jusqu'à la haute extensibilité de la zone nerompue; *e* – après rupture.

Le test de fatigue, effectué par sollicitation à la torsion du filament p.v.a. soluble, indique d'abord la séparation des filaments avant de rupture (Fig.5).

Le filament a été fatigué jusqu'à la rupture, sur un appareil Zwigler D 312 par

Fig. 5.– La fatigue effectuée par sollicitation à la torsion du fil filamentaire p.v.a. Solvron SX.

un cycle de 900 torsions/50 cm en sens Z et après 90 torsions/50 cm en sens S. On peut observer l'apparition de la rupture separément à chaque filament dans la Fig.5.

La forme de la rupture dans le cas des sollicitations à la torsion est compliquée par l'existence des grands tensions qui sont excercées et qui dégradent évidemment la surface de la fibre.

Une autre méthode d'observation du comportement du fil à la fatigue jusqu'à la rupture est la sollicitation à l'abrasion. Le frottement est un processus complexes qui est constitué dans le vaincrement des forces par suite des aspérités de la surface de la fibre et aussi des forces réciproques d'attraction physique qui apparaîssent entre les molecules qui sont en contact sur la surface des fibres. Par le test d'abrasion on peut évaluer la résistance à la surface des filaments. Pour ce test a été utilisé l'appareil Productimeter-Durant. Après 1760 cycles de frottement dans l'air (65% humidité relative et T=20°C), la rupture du fil a en place.

On peut observer dans la Fig.6 la présence de beaucoup de stries transversales en longueur du filament qui représentent les initiations de rupture. Le nombre des stries dépend des condition des sollicitations; si celles-ci sont sévères, les fissures sont plus profondes. Et dans ce cas on observe clairement le mode de la propagation de la rupture.

Fig. 6.– La rupture par abrasion du fil filamentaire p.v.a. Solvron SX (filament individuel).

Fig. 7.– Le filament individuel p.v.a. Solvron SX après un nombre de 500 de sollicitations cycliques.

On a illustré aussi le comportment du fils filamentaire de type p.v.a. soumis à l'un nombre de 500 de sollicitations cycliques. Ce test a été effectué à l'aide d'appareil Statimat M. La Fig.7 montre une dégradation très profonde du filament, à observer par un grand nombre d'initiations de rupture.

Si la fatigue statique détermine une augmentation du défaut par concentration de tension à la limite de la néhomogénéité maximum de la fibre, la fatigue dynamique, par suite de récristallisation continue du polymère, un grand nombre de défauts sont developpés.

3. Conclusion. Dans cet article une étude a été réalisée de la structure et comportément à la fatigue et rupture des fibres et fils filamentaires de type p.v.a.

En même temps, des explications qualitatives ont été données, différentes formes de fatigue et du phénomène de rupture.

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COMPORTAREA LA OBOSIRE ŞI RUPERE
A FIBRELOR ŞI FIRELOR DE TIP P.A.V.

(Rezumat)

Se urmăreşte realizarea unui studiu de structură şi investigarea fenomenelor de obosire şi rupere ale fibrelor şi firelor filamentare de tip polialcoolvinilic.

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KINETISCHE ASPEKTE DER BINDUNG VON DIAZONIUMSALZEN AN DAS WOLLKERATIN

VON
SAVEL IFRIM

1. Einleitung. Die Anwendung von Diazoniumsalzen in der Wollchemie ist schonseit langer Zeit bekannt; auf sie stützt sich die Reaktion von P a u l y [1], die zum Nachweis des Wollfaserabbaus und zur vergleichenden Bestimmung dieses Abbaus dient. Die Reaktion von P a u l y beruht auf der Eigenschaft des Thyrosins aus dem Wollkeratin, sich an Diazoniumsalze anzulagern, was zum Färben dieses proteinartigen Stoffes führt.

Die Diazoniumkationen, wie auch andere Kationen übrigens, sind elektrophile Reaktionspartner und folglich werden sie das Auslösen von elektrophilen Substitutionreaktionen bei den aromatischen Kernen, die sich frei in der chemischen Struktur des Wollkeratins befinden, bedingen.

Es ist allgemein bekant, daß Keratin außer dem Thyrosin auch andere Aminosäuren enthält, deren chemischer Aufbau aromatische Kerne aufweist, und zwar: Phenylalanin, Tryptofan und Histidin. Neuere Forschungen [2] haben gezeigt, daß alle diese vier Aminosäuren, Thyrosin, Phenylalanin, Tryptofan und Histidin, sich an die Diazoniumsalze anlargen, wobei sie Azofarbstoffe bilden. Demnach nehmen alle vier aromatischen Kerne an elektrophilen Substitutionsreaktionen teil. Diese elektrophilen Substitutionsreaktionen finden nicht nur dann statt, wenn diese Kerne isoliert sind, sondern auch dann, wenn sie an makromolekularen Strukturen teilnehmen wie z.B. die polypeptidischen Strukturen, auf denen die Proteinfasern beruhen.

Zweck dieser Arbeit ist, den kinetischen Vorgang der Bindung von Diazoniumkationen an die Wollfaser zu verfolgen und festzustellen, ob eine Abhängigkeit zwischen dem chemischen Aufbau des Kations und der Reaktionsgeschwindigkeit mit dem Wollkeratin besteht.

2. Theoretischer Teil. Die Wollfaser ist ein biologisches proteinartiges Zellenprodukt, das einen sehr komplexen histologischen Aufbau besitzt. Der Proteinstoff, auf dem die Wollfaser beruht, das Keratin, ist eine makromolekulare Substanz von ebenfalls sehr komplexer Struktur. Diese Komplexität wird sowohl durch die große Anzahl von unterschiedlichen, an der Bildung der Polypeptidketten teilnehmenden Aminosäuren bestimmt, als auch durch die räumliche Ausrichtung dieser Ketten

und ihrer seitlichen Reste.

Die aromatischen Kerne aus der Zusammensetzung des Phenylalanins, Thyrosins, Tryptofans und Histidins gehören zur Kategorie der seitlichen Reste der makromolekularen Polypeptidketten. Weil diese Reste frei sind, werden sie, gemäss ihrer chemischen Struktur, an verschiedenen chemischen Reaktionen teilnehmen. Es ist somit selbstverständlich, daß die seitlichen Reste mit aromatischen Kernen an elektrophilen Substitutionsreaktionen teilnehmen. Behandelt man die Wollfaser mit Diazoniumsalzen, dann werden die Kationen dieser Salze – als elektrophile Reaktionspartner – die aromatischen Kerne angreifen und durch Anlagerung Azofarbstoffe bilden, so daß sich die Wolle färben wird. Man kann behaupten, daß unter diesen Bedingungen die Wolle die Rolle einer Anlagerungskomponente spielt.

Histologisch gesehen, unterscheidet man im Aufbau einer Wollfaser drei aus Keratin gebildete Hauptschichten:

– Die kutikuläre Schicht oder Kutikula befindet sich an der Oberfläche der Faser und hat ein charakteristisches Aussehen. Sie ist aus Schuppen gebildet, hat eine größere Dichte [3] und stellt sozusagen eine schützende Hülle für die gesamte Wollfaser dar. Man schätzt, daß die kutikuläre Schicht ungefähr 2-10% vom Gewicht der Faser ausmacht [4].

– Die kortikale Schicht oder Rinde (Kortex) ist die wichtigste Komponente der Wollfaser und beträgt ungefähr 90% von der Fasermasse. Der Kortex bildet den eigentlichen Körper der Faser und bestimmt in hohem Grade die physikalisch-mechanischen und chemischen Eigenschaften der Faser.

– Die meduläre Schicht, auch Markkanal genannt, befindet sich im Innern der Faser. Bei den feinen Wollarten ist diese Schicht sehr gering und kann sogar fehlen. In vorliegender Arbeit wird der Markkanal nicht in Betracht gezogen.

Alle diese Schichten sind organisch miteinander verbunden und bilden die Wollfaser. Das zum Inhalt der Kutikula gehörende Keratin ist nicht identisch mit demjenigen der Medula. Es unterscheidet sich durch die Zusammensetzung hinsichtlich der α-Aminosäuren und folglich durch physikalische und chemische Eigenschaften. Es ist bekannt, daß in der kutikulären Schicht kein Thyrosin vorhanden ist und daß sich, praktisch, der ganze Gehalt an Thyrosin aus der Wollfaser im Kortex befindet. Auch andere Aminosäuren mit aromatischen Kernen in ihrer chemischen Zusammensetzung sind in der Kutikula nicht zu finden [5]...[7].

Die andern seitlichen Reste der Polypeptidketten enthalten verschiedene polare Gruppen [8], wie: Säuregruppen (Karboxyl-, Phenolgruppen), basische Gruppen (Imin-, Amin-, Gaunidingruppen) oder andere Gruppen (Alkohol-, Thiol-, Amidgruppen). Alle diese Gruppen sind polare Gruppen und besitzen hydrophile Eigenschaften, folglich können sie in Zwischenbeziehungen zum Wasser treten, entweder mittels Wasserstoffbrücken [9] oder durch Ion-Dipol-Zwischenbeziehungen. Mit Hilfe der Wassermoleküle dringen ins Innere der Wollfaser auch die Diazoniumkationen ein, da sich zwischen diesen Kationen und den Wassermolekülen Ionen-Dipol-Zwischenbeziehungen bilden. Wir müssen annehmen, daß ein Diffusionsvorgang in zwei Etappen verläuft: die erste Etappe besteht aus der Diffusion der Diazoniumkationen durch die Lösung zur Faseroberfläche hin, während in der zweiten Etappe

die Diazoniumkationen, gleichzeitig mit den Wassermolekülen, durch die Wollfaser in Richtung Inneres diffundieren. Daraus ist ersichtlich, daß sich die Anlagerungareaktion der Diazoniumkationen an die aromatischen Kerne nicht in allzu kurzer Zeit vollzieht.

Andererseits ist es nicht notwendig, daß die kutikuläre Schicht zerstört wird, um das Eindringen der Diazoniumsalze in die Faser zu fördern. Es ist genügt, die Wollfaser einem einfachen Schwellungsprozess zu unterwerfen, wobei sich die Schuppen ein wenig vom Kortex entfernen – so wie man es mit dem Mikroskop beobachten kann und die chemischen Reagenzien dringen viel leichter ein. Diese Quellung findet in wässriger Umgebung statt, wobei die kleinen Wassermoleküle zwischen die Polypeptidmakromoleküle eindringen. Die von der Wasserabsorption bestimmte Quellung der Wollfaser wird durch die Anwesenheit von voluminösen Ionen [10] nicht beeinflusst. Durch das Quellen im wasserhaltigen Medium vergrößert sich der Faserdurchmesser um 18%.

Da man von einer Absorptionskinetik des Wassers von seiten der Wollfaser sprechen kann [11], [12], erscheint es als logisch, auch eine Kinetik der Bindung der Diazoniumkationen durch diesen Faserstoff zu verfolgen. Zu diesem Zweck wurden die Wollproben in wässrigen Lösungen von Natriumkarbonat gehalten, um die Quellung hervorzurufen. Danach schüttete man über diese Proben Diazoniumsalzlösungen, deren Konzentration sehr genau bekannt war. Nach gewissen Zeitspannen wurde durch Titration mit β-Naphthollösungen der Diazoniumsalzerest, der sich nicht ans Keratin angelagert hatte, bestimmt. Diese Versuche wurden bei kalter Temperatur durchgeführt. Aus dem Verbrauch an β-Naphtol wurde die an die Wollfaser angelagerte Menge von Diazoniumsalz berechnet; gleichlaufend wurden auch Kontrollproben erarbeitet.

3. Experimenteller Teil. Im Labor verfolgte man die Kinetik der Diazoniumsalzbindung durch das Keratin. Diese Diazoniumsalze wurden durch Diazotierung von Anilin, Para-Nitroanilin und α-Naphthilamin erhalten. Dieser Vorgang wurde für folgende Zeitspannen des Kontaktes zwischen Keratin und den Lösungen dieser Salze beobachtet: 10, 20, 30, 60, 120 und 180 Minuten.

Praktisch wurden auf der analytischen Waage Wollproben von je 0,5 g gewogen und in Berzeliusgläschen, die je 50 ml 1%-iger Lösung von kristallisiertem Natriumkarbonat enthielten, eingeführt; der pH-Wert dieser Lösung betrug 11. Jede Probe wurde in diesen Lösungen 60 Minuten lang, bei einer Temperatur von 3-4°C gehalten. Das basische Medium wie auch die niedrige Temperatur sind notwendige Bedingungen nicht nur für den Quellungsvorgang der Faser, sondern auch für die Auslösung der Anlagerungsreaktion zwischen Keratin und Diazoniumkationen.

Bei der Diazotierung von Analin, *Para*-Nitroanalin und α-Naphthilamin wurden die Anleitungen aus der Fachliteratur [13] befolgt. Für jedes diazotierbares Amin wurden 500 ml Diazoniumlösung, genau 0,1 molar, hergestellt. Für die Diazotierungsreaktion gebrauchte man stöchiometrische Mengen von Natriumnitrit und Salzsäure. Die ganze Zeit über wurden die Diazoniumsalzlösungen im Kalten gehalten, bzw. bei Temperaturen unter 5°C.

Die Herstellung der der Titration der nicht mit dem Keratin verbundenen Dia-

zoniumkationen notwendigen 0,1 molare β-Naphthollösung wurde ebenfalls gemäss der Anleitungen aus dur Fachliteratur vorgenommen. Nach der Herstellung wurde auch diese Lösung bis zu einer Temperatur von 3-4°C abgekühlt. Jedes Mal, unter Anwendung des Ergebnisses der Kontrollprobentitration, wurde der Faktor der β-Naphthollösung bestimmt, weil sie ein technisches Erzeugnis ist und das Abwiegen auf der analytischen Waage überflüssig war.

Nachdem die Wollprobe von 0,5 g genau 60 Minuten in der Natrium karbonatlösung aufbewahrt wurde, führte man über sie 50 ml von einer Lösung von diazotiertem Amin ein, indem man die entsprechende Menge mit einer Messpipette bestimmte. Nach Zeitspannen von 3 Minuten wurde gerührt und darauf geachtet, daß die Temperatur der Lösung aus dem Anlagerungsbecher nicht über 4°C steigt.

Für jede Zeitspanne, während der sich die Diazoniumsalzlösung in Kontakt mit der Wolle befand, wurden getrennte Proben gemacht. Nachdem die vorgesehene Zeit verflossen war, zog man die Wollprobe heraus und wusch sie mit destilliertem Wasser. Von der zurückgebliebenen Lösung, in der freies Diazoniumsalz, das an der Anlagerungsreaktion an Keratin nicht teilgenommen hatte, vorhanden war, wurden mit einer Messpipette je 25 ml entnommen und mit der β-Naphthollösung titriert. Die Festlegung des Äquivalenzpunktes der Anlagerungsreaktion zwischen Diazoniumsalz und β-Naphthol erfolgte durch die Durchführung von Anlagerungsproben auf Filterpapier, wobei man eine alkalische Lösung von 1%-iger H-Säure benutzte. Es ist bekannt, daß sich die H-Säure leicht an die Diazoniumsalze auf Filterpapier anlagert. Als Äquivalenzpunkt dieser Anlagerungsreaktion wurde der Augenblick betrachtet, in dem bei der Interferenz eines Tropfens der die Wollprobe enthaltenden Lösung mit einem Tropfen der β-Naphthollösung keine Färbung erscheint.

Davon ausgehend, daß Fehler auftreten könnten, wiederholte man die experimentellen Proben mehrmals, wobei jedes Ergebnis den Durchschnitt von 5 Bestimmungen darstellte.

Für jeden Fall wurden auch Kontrollproben gemacht. Zu diesem Zweck mischte man 50 ml Diazoniumsalzlösung mit 50 ml 1%-iger Natriumkarbonatlösung. Aus diesem Gemisch entnahm man für die Titration mit β-Naphthol ebenfalls je 25 ml. Das Ergebnis dieser Titration benutzte man zur Berechnung des Faktors der β-Naphthollösung mit Hilfe des Äquivalentengesetzes.

Die erzielten praktischen Daten wurden in die folgenden drei Tabellen eingetragen:

- Tabelle 1 enthält die Ergebnisse der Titration mit Benzoldiazoniumchlorid;
- Tabelle 2 für *p*-Nitrophenildiazoniumchlorid und
- Tabelle 3 für α-Naphthyldiazoniumchlorid.

4. Diskussion. Aus der Fachliteratur geht hervor [14], daß Phenylalanin in der Wollfaser in einem Verhältnis von über 4%, Thyrosin von über 6% und Tryptofan von über 2% vorkommen. Folglich überschreitet der gesamte Prozentsatz von Aminosäuren, die an der Anglagerungsreaktion teilnehmen könen, 12%. Dieser Prozentsatz ist hoch genug, um anzunehmen, daß die Wolle die Rolle einer Anlagerungskomponente spielen kann.

Tabelle 1

Dauer der Behandlung (Minuten)	Nr. ml der gebrauchten β-Naphthollösung mit f=0,51	Nr. ml. β-Naphthollösung genau 0,1 molar	Differenz gegenüber Kontrollprobe in ml	Menge, in g, der von 0,5 g Wolle gebundenen Diazoniumkationen	Menge, in g, der von 100 g Wolle gebundenen Diazoniumkationen
Kontrollprobe	24,4	12,45	–	–	–
10	23,2	11,83	0,62	0,00651	1,30
20	22,8	11,63	0,82	0,00861	1,72
30	22,5	11,47	0,98	0,0103	2,06
60	22,3	11,37	1,08	0,0113	2,26
120	22,2	11,32	1,13	0,0119	2,38
180	22,2	11,32	1,13	0,0119	2,38

Tabelle 2

Dauer der Behandlung (Minuten)	Nr. ml der gebrauchten β-Naphthollösung mit f=0,36	Nr. ml. β-Naphthollösung genau 0,1 molar	Differenz gegenüber Kontrollprobe in ml	Menge, in g, der von 0,5 g Wolle gebundenen Diazoniumkationen	Menge, in g, der von 100 g Wolle gebundenen Diazoniumkationen
Kontrollprobe	35	12,60	–	–	–
10	33,7	12,13	0,47	0,00705	1,41
20	33,0	11,88	0,72	0,0108	2,16
30	32,7	11,77	0,83	0,0125	2,50
60	32,1	11,56	1,04	0,0156	3,12
120	32,1	11,56	1,04	0,0156	3,12
180	32,1	11,56	1,04	0,0156	3,12

Die aus den oben beschriebenen Versuchen hervorgegangenen Muster von gefärbter Wolle erscheinen nach dem Trocknen stärker gefärbt je länger sie in Berührung mit den Diazoniumsalzen waren. Diese Tatsache erlaubt uns die Einschätzung, daß die Diffusion der Diazoniumkationen in Richtung Faserinneres sowie auch ihre Anlagerung an die aromatischen Kerne längere Zeit in Anspruch nimmt.

Mit Hilfe der experimentellen Daten wurden die Kurven aus den folgenden Abbildungen aufgezeichnet. Sie widerspiegeln den Vorgang der Rückhaltung der Diazoniumkationen durch das Wollkeratin in Abhängigkeit von der Zeit.

– Die Kurve aus Abb. 1 zeigt die Kinetik der Bindung von Benzoldiazoniumkationen.

Tabelle 3

Dauer der Behandlung (Minuten)	Nr. ml der gebrauchten β-Naphthollösung mit f=0,54	Nr. ml. β-Naphthollösung genau 0,1 molar	Differenz gegenüber Kontrollprobe in ml	Menge, in g, der von 0,5 g Wolle gebundenen Diazoniumkationen	Menge, in g, der von 100 g Wolle gebundenen Diazoniumkationen
Kontrollprobe	23,1	12,47	–	–	–
10	22,8	12,31	0,16	0,00248	0,496
20	22,4	12,10	0,37	0,00574	1,148
30	21,8	11,77	0,70	0,01085	2,170
60	21,1	11,39	1,08	0,01674	3,348
120	21,1	11,39	1,08	0,01674	3,348
180	21,1	11,39	1,08	0,01674	3,348

– Die Kurve aus Abb. 2 zeigt die Kinetik der Bindung von *p*-Nitrophenyldiazoniumkationen.

– Die Kurve aus Abb. 3 zeigt die Kinetik der Bindung von α-Naphthildiazoniumkationen.

In allen Fällen zeigt die Ordinate die Menge der Diazoniumkationen in Gramm an, und die Abszisse die Reaktionsdauer in Minuten.

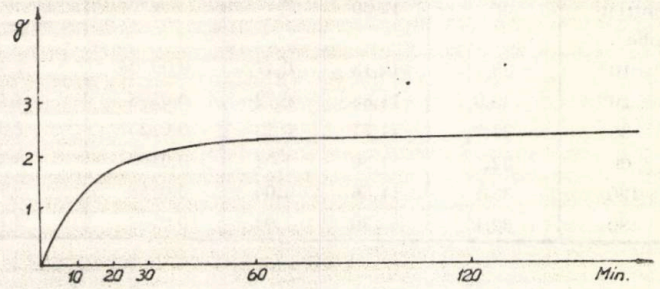

Abb. 1

Analysiert man die Daten aus den drei Tabellen sowie auch den Verlauf der den kinetischen Vorgang widerspiegelnden Kurven, kann man bewerten, daß in allen Fällen die größte Menge von Diazoniumkationen in den ersten 60 Minuten gebunden wird. Verlängert man die Dauer des Kontaktes zwischen Wolle und Diazoniumsalze über 60 Minuten, wächst die an das Keratin angelagerte Menge von Diazoniumkationen bis zur Dauer von 120 Minuten nicht mehr oder sehr wenig, wie im Falle des Benzoldiazoniumchlorids.

Beibachtet man die Daten der Tabellen und den Verlauf der Kurven aus den drei Abbildungen, kann man leicht feststellen, daß sich in den ersten 30 Minuten

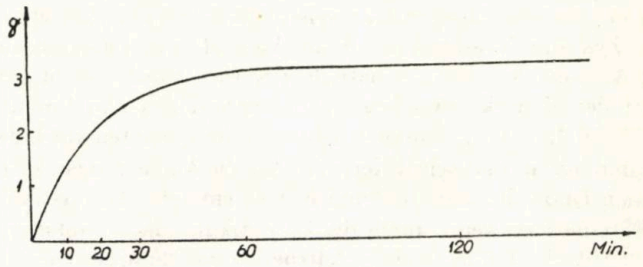

Abb. 2

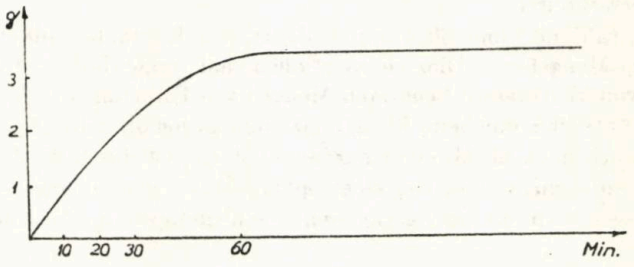

Abb. 3

die *p*-Nitrobenzoldiazoniumkationen mit größerer Geschwindigkeit ans Keratin binden. Diese Erscheinung ist nicht zufällig; sie wird durch die Anwesenheit der $-NO_2$ Gruppe (Nitrogruppe) im Kationmolekül erklärt. Diese Gruppe bedingt durch ihren -I-Effekt das Anziehen der Elektronen, was zum Wachsen der kationischen (positiven) Ladung führt. Aus diesem Grunde wird das *p*-Nitrophenyldiazoniumkation ein stärkerer und reaktiver Reaktionspartner, so das es in den ersten Minuten des Kontaktes mit dem Keratin in größeren Mengen gebunden wird.

Beim α-Naphthildiazoniumkation ist die in den ersten 20 Minuten gebundene Quantität viel geringer als im Falle der anderen 2 Kationen. Diese schwächere Reaktionsgeschwindigkeit kann mit Hilfe der histologischen Struktur der Wollfaser und des Volumens des α-Naphthildiazoniumkations erklärt werden. Im Vergleich zu dem Volumen der andern zwei verwendeten Kationen ist dasjenige des α-Naphthildiazoniumkations größer, was für die Diffusion in Richtung Kortex ein Hindernis darstellt. Diese Behinderung der Diffusion kann der Eigenschaft der Epikutikula, welche die Schuppen bedeckt, zugeschrieben werden. Einige Forscher sind der Meinung [15], daß die Epikutikula die Rolle einer halbdurchlässigen Membrane spiele. Auf diese Eigenchaft der Epikutikula stützt sich auch die Behauptung, daß sie das Eindringen der größeren Moleküle in die Faser beeinflusse [16]. Wahrscheinlich wird das Eindringen der Moleküle in die Wollfaser von der gesamten Kutikula geregelt, die – wie bekannt – eine größere Dichte aufweist.

Die von Z a h n [17] und andern Forschern durchgeführten Analysen der Aminosäuren, die am Aufbau der Epikutikula teilnehmen, konnten Allanin, Arginin und

Threonin in kleineren Mengen nachweisen, Lyzin und Glykokoll in größeren Mengen, dann Zystin, Glutaminsäure, Serin, Valin, Lyzin, Threonin und α-Aminoadipinsäure; Aminosäuren mit aromatischen Kernen wurden nicht vorgefunden. Folglich führt der Kontakt zwischen Diazoniumkationen und Epikutikula nicht zur Bindung dieser Kationen. Übrigens fehlen in der gesamten kutikularen Schicht die Aminosäuren mit aromatischen Keren, so daß die Anlagerungsreaktion beim Kontakt zwieschen Diazoniumkationen und Kortex entsteht. Das α-Naphthildiazoniumkation diffundiert schwerer durch die Epikutikula, da es umfangreicher ist. Man beobachtet jedoch, daß nach einer Zeitspanne von 20 Minuten, Zeit genug für die Diffusion des α-Naphthildiazoniumkations in Richtung Faserinneres, die gebundene Menge merklich steigt und die Quantität der *p*-Nitrophenyldiazoniumkationen sogar überschreitet.

Die während eines 60 Minuten dauernden Kontaktes mit der Wollfaser gebundenen Mengen von Diazoniumkationen sind vergleichbar mit den laufend zum Färben von Textilfasern benutzten Mengen von Farbstoffen (3%).

Die Tatsache, daß beim Phenyldiazoniumkation die gebundene Menge geringer ist und auch nach 60 Minuten nur wenig steigt, ist durch die Eigenschaft dieses Kations, ein weniger reaktiver elektrophiler Substituent zu sein, erklärlich. Dieses Kation lagert sich mit einer geringeren Geschwindigkeit an die aromatischen Kerne an.

Zieht man in Betracht, daß es im Keratin einen hohen Anteil von Aminosäuren mit aromatischen Kernen gibt, wäre zu erwarten, daß sich eine größere Menge von Diazoniumkationen anlagern würde. Daß diese Menge kleiner als die theoretisch berechnete ist, die auch über 6% darstellen könnte, darf, unserer Meinung nach, sterischen Hindernissen sowie auch der Zugänglichkeit der Reaktionspartner zugeschrieben werden. So ist Tryptofan an zwei verschiedenen Stellen der Wollfaserstruktur anzutreffen [18]. In einem der Fälle befindet sich Tryptofan im äusseren morphologischen oder interzellulären Teil der Wolle und ist für die chemischen Reagenzien leicht zugänglich; im zweiten Fall liegt es jedoch im Innern der kortikalen Zellen und wird dadurch schwerer von den reaktionsfähigen Verbindungen angegriffen [19].

5. Zusammenfasung. Vorliegende Arbeit bezweckt, die Kinetik der Bindung von elektrophilen Reaktionspartnern, wie die aus der Diazotierung von Anilin, *p*-Nitroanilin und α-Naphthilamin hervorgegangenen Diazoniumkationen, ans Keratin zu verfolgen.

Die Anwesenheit einer großen Anzahl von polaren, freien, Hydrophilen Gruppen in der chemischen Struktur des Keratins bestimmt das Eindringen der Wassermoleküle ins Faserinnere und zusammen mit ihnen auch der Diazoniumkationen. Das Schwellen der Faser im wässrigen Medium begünstigt die Diffusion dieser Kationen in die Faser.

Die experimentellen Daten sowie auch die praktischen Beobachtungen sind ein Beweis dafür, daß die Bindung der Diazoniumkationen durch das Keratin während einer größeren Zeitspanne vorsichgeht. Aus diesen Daten kann man ebenfalls folgern, daß die größte Menge von Diazoniumkationen in den ersten 60 Minuten ge-

bunden wird.

Vergleicht man die verschiedenen Geschwindigkeiten der Anlagerung von Diazoniumkationen, kann man schlußfolgern, daß das Kation von *p*-Nitrophenyldiazonium die höchste Reaktivität aufweist. Man bietet eine theoretische Erklärung für diese Reaktivität.

Daß in den ersten 20 Minuten eine kleinere Menge von α-Naphthildiazoniumkationen gebunden wird, ist der eigentümlichen histologischen Struktur der Wolle zuzuschreiben, sowie auch der Tatsache, daß dieses Kation, da es umfangreicher ist, schwerer durch die sich wie eine halbdurchlässige Membrane verhaltende Epikutikula dringt.

Das Phenyldiazoniumkation, das ein schwächerer elektrophiler Reaktionspartner ist, benötigt mehr Zeit, um sich ans Keratin anzulagern.

Die in Gramm gemessene, vom Keratin gebundene Menge von Diazoniumkationen ist der bei den gewöhnlichen Färbevorgängen benutzten Farbstoffmenge vergleichbar.

Man schätzt, daß der vom Keratin festgehaltene Prozentsatz von Diazoniumkationen den theoretisch berechneten nicht erreicht, und zwar infolge der sterischen Hindernisse und der Zugänglichkeit der Reaktionspartner.

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ASPECTE CINETICE ALE LEGĂRII SĂRURILOR DE DIAZONIUM DE CHERATINA LÂNII

(Rezumat)

Se urmăreşte cinetica legării de către cheratina lânii a cationilor de diazonium, rezultaţi prin diazotarea anilinei, *p*-nitroanilinei şi α-naftilaminei.

Grupele hidrofile existente în structura chimică a cheratinei determină pătrunderea moleculelor de apă în interiorul fibrei şi prin intermediul lor pătrund şi cationii de diazonium. Umflarea fibrei în mediu apos favorizează difuzia acestor cationi în fibră.

Datele experimentale demonstrează că legarea cationilor de diazonium de către cheratină are loc într-un timp mai îndelungat şi că cea mai mare cantitate din cationii de diazonium se leagă în primele 60 de minute.

Observaţiile comparative ale vitezei de legare a cationilor de diazonium duc la concluzia că cel mai reactiv este cationul de *para*-nitrofenildiazonium.

Datorită structurii histologice a fibrei de lână şi volumului mai mare a cationului de α-naftildiazonium, acesta pătrunde mai greu prin epicuticulă, care joacă rol de membrană semipermiabilă. Cationul de fenildiazonium se leagă de cheratină într-un timp mai îndelungat.

Cantitatea de cationi de diazonium legată de cheratină este comparabilă cu cantitatea de coloranţi ce se folosesc pentru vopsirea obişnuită.

Se interpretează că datorită împiedicărilor sterice, cât şi accesibilităţii reactanţilor, procentul de cationi de diazonium reţinut de cheratină nu atinge procentul ce rezultă prin calcul teoretic.

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Secţia VIII
TEXTILE. PIELĂRIE

WOOL'S GRAFTING THROUGH INITIATION WITH UV RADIATIONS

I. ESTABLISHMENT OF THE OPTIMUM CONDITIONS FOR GRAFTING WITH ALKYL-ACRYLIC MONOMERS

BY

AURELIA GRIGORIU, V. BLAŞCU,
ADRIANA GRECU and ELENA COSTEA

1. Introduction. Starting with 1944, when B a r r and S p e a k m a n performed the first reaction of wool's grafting [1], until the present time, several studies have been devoted to such problems [2]. However, on considering the wool fiber's chemical and morphological complexity, the problems are far from being "exhausted"; moreover, some new aspects may appear, contributing to a better understanding of the reactions' chemistry or to improving, in unexpected ways, some of wool's characteristics.

Out of the large range of monomers involved in wool's grafting, the acrylic ones have been less employed, while the alkyl-acrylates and hydroxyalkyl-acrylates – considered in our studies – have been never utilized before.

To this end, several methods for the initiation of grafting processes (including various redox systems, UV or γ irradiation, or effluent electron flows) have been applied to a large range of vinylic and allylic monomers [2].

Initiation of wool's grafting through UV has been less studied up to now [3],...,[5], probably because of the lower efficiency of the method – comparatively with that attained by other procedures – as well as of the difficulties involved by the selection of the most suitable systems of photosensitizers, superphotosensitizers and thermic inhibitors.

UV radiation initiation – whether selected and controlled adequately – has the advantage of a minimum degradation of the wool fiber, comparatively with other procedures – especially the ones using γ radiations or redox systems [6],...,[10].

2. Experimental. UV initiated graftings have been applied to Romanian semifine wool fibers of the 22 type, with three alkyl-acrylic monomers of a homologous series (Table 1) having been employed (the methyl-acrylate, studied previously by H.L.N e e d l e s [4],[5], has not been utilized any more).

2.1. Materials. The wool samples (in the form of tops), free of any impurities, has been cleaned with ethylic ether in a Soxhlet extractor, for 24 h, followed by

Table 1

Acrylic-Alkyl Monomers Employed in Reactions of Wool's Grafting

Monomer	Chemical formula	Symbol
Ethyl acrylate	$CH_2 = CH$ | $COO-CH_2-CH_3$	EA
n-Propyl acrylate	$CH_2 = CH$ | $COO-CH_2-CH_2-CH_3$	PA
n-Butyl acrylate	$CH_2 = CH$ | $COO-CH_2-CH_2-CH_2-CH_3$	BA

conditioning in a dessicator (65% RH, t=22°C).

The monomers have been distilled in vacuum, with an inert gas, for removing the inhibitors. Benzene, employed as a solvent, has been anhydrized on metallic natrium, then distilled in vacuum.

Based on literature data, the following substances have been selected [6], [7]:

– benzyldimethylketal (Irgacure 651 – Ciba Geigy), photosesitizer, melting point = 65°C, soluble in benzene;

– 4,4'-bis dimethylaminobenzofenone (Michler's ketone, Merck), superphotosensitizer, melting point = 175°C, soluble in benzene;

– 4-metoxyphenol (Merck), thermic inhibitor, melting point = 56°C, soluble in benzene.

The UV source emploed was a UV-IR lamp, 280 W power, STAS 9057-71, with screened IR radiations.

2.2. Method. It is known that the power of the radiation flow decreases with increasing the distance between the source and the sample. Measurements of the UV radiation ($\lambda = 365$ nm) power, at different distances from the source, evidenced as the most suitable a 20 cm distance between the source and the sample, when the sample's heating is minimum and the UV radiation power is maintained at quite a high level, of 1.1 mW/cm^{2}sec.

Measurements of the fibers' diameter were performed on a Lanameter with a magnification degree of 500x.

Determinations of resistance and of relative elongation to breaking were made on a Digital Electronic Tester FM-27 dynamometer.

While characterization of the reference wool sample involved determinations of:

– average diameter ($\overline{d}$, μm) as the average value of 500 measurements on the Lanameter, the value of $\overline{d} = 22.64$ μm being obtained;

– average breaking force ($\overline{P}_r$, g/fiber) and average relative elongation at breaking ($\overline{\varepsilon}_r$, %), as average values of 100 trials on the dynamometer; the value of $\overline{P}_r = 12.10$ g/fiber and $\overline{\varepsilon}_r = 26.47\%$ being obtained.

In order to find out the optimum reaction parameters and to study the way in which they influence the process, a series of experiments have been performed,

according to a centered, rotatory, complex, second order programme [11],...,[14].

The independent variables selected are the following: volume of monomer (x_1, mL), time of irradiation (x_2, minutes) and amount of photosensitizer (x_3, grams). In all experiments, 0.016 g of superphotosensitizer, 0.004 g thermic inhibitor, 0.15 g wool and 10 m solvent have been introduced.

The samples immersed in the reaction mixture and put on a watch glass have been UV irradiated – according to the experimental program – for variable durations of time. After grafting, the fibers have been subjected to extractions for the removal of the benzene – containing homopolymer, for 6 hours, followed by drying at room temperature and conditioning, for 48 h, in a dessicator (65% RH, $t = 22°C$) in weighing vials the weights of which had been previously determined. Finally, the weight of the conditioned samples have been determined.

3. Results and Discussion. The values of the reaction parameters (independent variables) have been coded according to Table 2.

Table 2

Real and Coded Values of the Parameters of the Wool-Alkyl Acrylic Monomer Grafting Reaction

Real variable	Coded variable				
	−1.682	−1	0	1	1.682
x_1, mL monomer	0.5	0.8	1.25	1.7	2
x_2, minutes	13	20	30	40	47
x_3, g photosensitizer	0.0800	0.1043	0.1399	0.1755	0.2000

As response functions (Y), there have been selected:

– the degree of grafting (G, %), determined gravimetrically with the following relation:

$$G = \frac{M_f - M_i}{M_i} \times 100,$$

where: M_i – weight of the wool fibers before grafting (0.15 g); M_f – weight, in grams, of the grafted wool fibers, after the homopolymer's extraction;

– average diameter, ($\overline{d}$, μm), determined as the average value of 100 measurements per sample;

– the average breaking force ($\overline{P}_r$, g/fiber) representing the average value of 50 determinations/samples;

– average relative elongations at breaking ($\overline{\varepsilon}_r$, %), representing the average value of 50 determinations/sample.

The experimental schedule and the obtained results are presente Tables 3, 4 and 5.

In order to correlate the response functions with the parameters had in view, a equation of the following type has been proposed:

$$Y = a_0 + a_i x_i + a_{ij} x_i x_j \qquad i \leq j,$$

Table 3

Experimental Schedule and Obtained Results for Ethyl Acrylate

Nr.	Coded variable			G, [%]		$\overline{d}$, [μm]		$\overline{P}_r$, [g/fb]		$\overline{\varepsilon}_r$, [%]	
	x_1	x_2	x_3	real	calculated	real	calculated	real	calculated	real	calculated
1	−1	−1	−1	14.16	15.86	25.62	25.72	17.72	18.14	26.33	26.54
2	1	−1	−1	18.31	22.73	27.24	27.73	19.57	21.43	27.37	27.61
3	−1	1	−1	17.60	21.31	26.56	27.43	19.63	20.73	27.18	27.19
4	1	1	−1	30.77	30.81	30.40	30.51	24.10	24.11	29.16	29.07
5	−1	−1	1	16.70	19.46	26.44	27.01	18.81	19.77	26.98	27.24
6	1	−1	1	29.88	28.97	30.21	30.03	23.40	23.27	28.01	28.17
7	−1	1	1	27.98	26.35	28.40	28.59	23.18	22.29	27.94	27.88
8	1	1	1	37.41	38.51	32.12	32.69	25.32	25.87	29.66	29.62
9	−1.682	0	0	16.50	13.95	26.41	25.71	18.10	17.68	26.83	26.65
10	1.682	0	0	31.37	29.95	31.12	30.85	24.30	23.40	29.10	29.01
11	0	−1.682	0	23.72	20.32	27.27	27.00	21.73	20.34	27.56	27.13
12	0	1.682	0	33.48	32.92	31.38	30.68	24.70	24.70	28.71	28.89
13	0	0	−1.682	28.56	24.04	28.48	27.87	23.31	21.76	27.70	27.55
14	0	0	1.682	32.97	33.53	31.14	30.78	24.45	24.62	28.72	28.60
15	0	0	0	30.38	30.52	30.43	30.45	24.06	24.07	28.96	28.60
16	0	0	0	30.41	30.52	30.45	30.45	24.01	24.07	28.96	28.60
17	0	0	0	30.43	30.52	30.46	30.45	24.05	24.07	28.93	28.60
18	0	0	0	30.45	30.52	30.46	30.45	24.10	24.07	29.01	28.60
19	0	0	0	30.42	30.52	30.40	30.45	24.04	24.07	28.92	28.60
20	0	0	0	30.40	30.52	30.39	30.45	24.00	24.07	28.94	28.60

where: Y – response function; x_i, x_{ij} – variables representing the parameters had in view; a_i, a_{ij} – regression coefficients.

The establishment of the regression coefficients of the above-mentioned equation was made by the method of multiple regression.

The response functions (Y) obtained for the 4 dependent variables and for the 3 monomers are the following:

for ethyl acrylate:

$$G,\ [\%]\quad Y = 26.654 + 4.760x_1 + 3.890x_2 + 2.838x_3 - 2.949x_1^2 - 1.473x_2^2 - 0.650x_3^2 + 0.597x_1x_2 + 0.86x_1x_3 + 0.47x_2x_3$$

$$\overline{d},\ [\mu\text{m}]\quad Y = 28.542 + 1.427x_1 + 1.425x_2 + 0.802x_3 - 1.094x_1^2 - 0.785x_2^2 - 0.693x_3^2 + 0.642x_1x_2 + 0.354x_1x_3 - 0.0475x_2x_3$$

$$\overline{P}_r,\ [\text{g/fb}]\quad Y = 17.155 + 1.559x_1 + 1.61x_2 + 1.3x_3 - 0.515x_1^2 - 0.0606x_2^2 - 0.116x_3^2 + 0.686x_1x_2 + 0.6862x_1x_3 + 0.478x_2x_3$$

$$\overline{\varepsilon}_r,\ [\%]\quad Y = 25.975 + 0.6751x_1 + 0.6764x_2 + 0.5873x_3 - 0.3381x_1^2 - 0.2567x_2^2 - 0.1153x_3^2 + 0.2675x_1x_2 + 0.4774x_1x_3 + 0.28x_2x_3$$

Table 4

Experimental Schedule and Obtained Results for Propyl Acrylate

Nr.	Coded variable			G, [%]		$\overline{d}$, [μm]		$\overline{P}_r$, [g/fb]		$\overline{\varepsilon}_r$, [%]	
	x_1	x_2	x_3	real	calculated	real	calculated	real	calculated	real	calculated
1	−1	−1	−1	13.64	15.37	25.02	26.12	17.14	17.57	26.24	26.42
2	1	−1	−1	17.72	22.23	26.61	25.92	19.14	20.94	27.10	27.41
3	−1	1	−1	17.26	20.99	25.87	26.02	18.76	19.95	26.88	27.14
4	1	1	−1	30.17	30.25	29.70	29.88	23.54	23.53	28.84	28.90
5	−1	−1	1	16.11	18.85	25.92	27.02	18.24	19.26	26.46	26.84
6	1	−1	1	29.41	28.50	29.73	30.48	22.96	22.78	27.74	27.92
7	−1	1	1	27.58	25.89	28.06	30.01	22.58	21.77	27.62	27.76
8	1	1	1	36.87	37.95	31.80	32.16	24.89	25.47	29.34	29.60
9	−1.682	0	0	15.94	13.41	25.91	27.02	17.62	17.00	26.48	26.11
10	1.682	0	0	30.80	29.32	30.78	31.96	23.82	22.97	28.77	28.49
11	0	−1.682	0	23.19	19.74	26.82	26.13	21.18	19.81	27.30	26.88
12	0	1.682	0	32.96	32.41	31.20	32.06	24.16	24.07	29.14	28.91
13	0	0	−1.682	28.33	23.71	27.91	29.30	22.70	21.13	28.01	27.73
14	0	0	1.682	32.48	33.11	30.56	31.72	24.07	24.18	29.04	28.68
15	0	0	0	29.82	29.93	29.81	29.68	23.44	23.40	28.76	28.70
16	0	0	0	29.86	29.93	29.84	29.68	23.26	23.40	28.63	28.70
17	0	0	0	29.80	29.93	29.86	29.68	23.35	23.40	28.67	28.70
18	0	0	0	29.84	29.93	29.79	29.68	23.40	23.40	28.70	28.70
19	0	0	0	29.81	29.93	29.80	29.68	23.30	23.40	28.60	28.70
20	0	0	0	29.83	29.93	29.82	29.68	24.46	23.40	28.79	28.70

for n-propyl acrylate:

$$G,\ [\%] \quad Y = 29.482 + 4.732x_1 + 3.759x_2 + 2.783x_3 - 1.357x_1^2 - \\ - 1.357x_2^2 - 0.519x_3^2 + 0.617x_1x_2 + 0.697x_1x_3 + 0.357x_2x_3$$

$$\overline{d},\ [\mu\text{m}] \quad Y = 29.558 + 1.483x_1 + 1.061x_2 + 0.899x_3 - 0.8569x_1^2 - \\ - 0.630x_2^2 - 0.395x_3^2 + 0.3112x_1x_2 + 0.266x_1x_3 - 0.0336x_2x_3$$

$$\overline{P}_r,\ [\text{g/fb}] \quad Y = 22.8859 + 1.771x_1 + 1.173x_2 + 0.9x_3 - 1.282x_1^2 - \\ - 0.38x_2^2 - 0.346x_3^2 + 0.035x_1x_2 + 0.0274x_1x_3 + 0.0275x_2x_3$$

$$\overline{\varepsilon}_r,\ [\%] \quad Y = 28.063 + 0.655x_1 + 0.528x_2 + 0.189x_3 - 0.510x_1^2 - \\ - 0.282x_2^2 - 0.164x_3^2 + 0.308x_1x_2 + 0.141x_1x_3 + 0.173x_2x_3$$

Table 5

Experimental Schedule and Obtained Results for Butyl Acrylate

Nr.	Coded variable			G, [%]		$\overline{d}$, [μm]		$\overline{P}_r$, [g/fb]		$\overline{\varepsilon}_r$, [%]	
	x_1	x_2	x_3	real	calculated	real	calculated	real	calculated	real	calculated
1	−1	−1	−1	13.26	14.18	24.72	23.94	16.51	18.20	26.53	27.18
2	1	−1	−1	17.31	18.72	26.10	27.23	18.52	20.66	26.43	27.06
3	−1	1	−1	16.84	17.43	25.51	24.67	18.16	19.22	26.17	26.95
4	1	1	−1	29.77	28.76	29.20	30.24	22.93	23.12	28.13	29.83
5	−1	−1	1	15.72	16.82	25.64	26.70	17.60	19.40	25.74	24.66
6	1	−1	1	28.97	29.43	29.15	29.90	22.34	23.62	27.03	28.09
7	−1	1	1	27.14	28.43	27.36	28.61	21.98	22.60	26.90	27.63
8	1	1	1	36.45	35.16	31.05	32.04	24.24	26.18	28.60	29.48
9	−1.682	0	0	15.50	16.82	25.23	28.16	17.00	18.32	25.63	27.72
10	1.682	0	0	30.42	32.49	29.98	30.26	23.19	25.61	28.07	29.36
11	0	−1.682	0	22.76	24.16	26.17	28.28	21.55	24.22	26.56	27.28
12	0	1.682	0	32.51	34.08	30.32	29.13	23.74	25.48	28.43	29.16
13	0	0	−1.682	27.95	29.14	27.54	28.60	22.07	23.27	27.36	28.46
14	0	0	1.682	32.06	33.77	30.28	31.95	23.41	22.96	28.30	29.65
15	0	0	0	29.37	28.16	29.52	28.47	22.83	22.10	28.04	29.16
16	0	0	0	29.40	28.16	29.56	28.47	22.86	22.10	28.08	29.16
17	0	0	0	29.32	28.16	29.49	28.47	22.80	22.10	28.00	29.16
18	0	0	0	29.42	28.16	29.59	28.47	22.90	22.10	28.12	29.16
19	0	0	0	29.36	28.16	29.53	28.47	22.82	22.10	28.04	29.16
20	0	0	0	29.38	28.16	29.54	28.47	22.85	22.10	28.06	29.16

for n-butyl acrylate:

$$G,\ [\%] \quad Y = 29.608 + 4.627x_1 + 3.740x_2 + 2.809x_3 - 3.056x_1^2 - 1.247x_2^2 - 0.467x_3^2 + 0.656x_1x_2 + 0.661x_1x_3 + 0.353x_2x_3$$

$$\overline{d},\ [\mu m] \quad Y = 29.644 + 1.492x_1 + 1.105x_2 + 0.878x_3 - 0.737x_1^2 - 0.369x_2^2 - 0.396x_3^2 + 0.241x_1x_2 + 0.236x_1x_3 - 0.0013x_2x_3$$

$$\overline{P}_r,\ [g/fb] \quad Y = 23.282 + 1.647x_1 + 1.363x_2 + 1.039x_3 - 1.274x_1^2 - 0.549x_2^2 - 0.155x_3^2 - 0.108x_1x_2 - 0.0813x_1x_3 + 0.101x_2x_3$$

$$\overline{\varepsilon}_r,\ [\%] \quad Y = 28.239 + 0.833x_1 + 0.568x_2 + 0.300x_3 - 0.252x_1^2 - 0.358x_2^2 - 0.342x_3^2 + 0.1399x_1x_2 - 0.0351x_1x_3 + 0.06x_2x_3$$

As a particular case, besides the grafting degree, physico-mechanical parameters have also studied, which permitted a correlation between the properties of the grafted fibers and the variables of the grafting process.

The value of Y is calculated with a standard deviation of 0.38% and a confidence threshold of over 99.9% (the "F" test has a value of 5.72 for 9 variables and

19 degrees of liberty, which corresponds to a significance test $P = 0.001$, which finnally determines the confidence threshold (of 99.9%).

The coefficient of multiple correlation and the "F" factor have values of 0.915 and 5.72, respectively, which indicates that the above equation adequately describes the dependence of the amount of grafted polymer and physico-mechanical parameters on the reaction parameters.

By particularizing two of the variables of the regression equation (in the centre of the experimental domain or in other point), there can be obtained information on the influence of the third one upon the reaction.

The optimum conditions obtained for the 3 monomers are:

for ethyl acrylate, in coded variables: $x_1 = +1$; $-0.6 < x_2 < 0.8$; $-0.4 < x_3 < 0.2$; in real variables: 1.7 mL monomer; UV exposure time = 24 ÷ 38 minutes; 0.1256 ÷ 0.1470 g photosensitizer;

for n-propyl acrylate, in coded variables: $x_1 = +1$; $-1 < x_2 < 0$; $-1 < x_3 < 1.6$; in real variables: 1.7 mL monomer; UV exposure time = 20 ÷ 30 minutes; 0.1043 ÷ 0.2000 g photosensitizer;

for n-butyl acrylate, in coded variables: $x_1 = +1$; $-0.8 < x_2 < 1.6$; $0 < x_3 < 1.6$; in real variables: 1.7 mL monomer; UV exposure time = 22 ÷ 47 minutes; 0.1399 ÷ 0.2000 g photosensitizer.

4. Conclusion. The acrylic alkyl monomers from the homologous series taken into study evidence different behaviours in the reactions of wool's UV photoinitiated grafting.

A certain decrease of the grafting degree was observed with the increase of the carbohydrated chain from homologous series, probably due to an effect of steric hindrance in the reaction of grafted copolymerization (an aspect to be fully analyzed in a subsequent paper).

In grafting degrees obtained by wool's UV initiated grafting with the alkyl acrylic monomers considered for the study attain similar values with those offered by literature for other monomers and other methods recommended for the initiation of the grafting reaction.

The physico-mechanical parameters increase with increasing the grafting degree, which does not agree with some of the results given in literature for other wool-grafted monomers. However, in all cited cases of grafting, the breaking force records, in most cases, a certain decrease, which indicates a different mechanism for linking of the grafted polymer on the fiber.

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GREFAREA LÂNII PRIN INIŢIERE CU RADIAŢII UV

I. Stabilirea condiţiilor optime la grefarea cu monomeri alchil-acrilici

(Rezumat)

Se studiază grefarea pe lână semifină românească a 3 monomeri din serie omologă (acrilat de etil, de propil şi de butil) prin iniţiere neconvenţională – radiaţii UV.

Au fost stabilite, pe baza unui program experimental, cu 3 variabile, condiţiile optime de grefare.

Pentru fiecare monomer s-au stabilit câte 4 funcţii de răspuns (Y), respectiv: grad de grefare, diametrul mediu al fibrelor grefate, forţa medie la rupere şi alungirea relativă medie la rupere a fibrelor grefate.

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MODIFICATION THROUGH REDOX-INITIATED GRAFTING OF SOME TYPES OF NATIVE WOOL

BY

V. BLAŞCU and O. MÂLCOMETE

1. Introduction. Due to its special properties, wool is one of the most valuable raw materials of textile industry [1].

Nevertheless, its complex chemical and morphological structure raises, sometimes, difficult problems as to its processing. Wool complex structure and especially its bilateral asymmetry, is reflected in its physical, chemical and mechanical properties.

The morphology of the cortex, as well as the structure of its external surface are very different, depending on fibers origin.

Of special importance in wool chemical structure is the sulphur content varying from one breed to another, from the part of the body it comes from or even within the same fiber [2].

The total sulphur content of Merino sheep wool is of 3.6%, 80% of which is present as cystine, placed either as an inter- or intrachain bridge [3].

The cystinic bridge contributes to the consolidation and stability of the structural building, being highly sensible to the action of chemical and physical agents. Breaking of the –S–S– bond of cystine reduces the mechanical resistance and the capacity of elastic recovery, modifying concomitantly the processes of wool supracontraction and fixation [4].

Grafting with vinylic monomers permits the control of some wool properties, such as: colour and lustre, resistance to alkalies, acids and light, resistance to abrasion, burning, tinctorial affinity, electrostatic charge, elastic recovery, rigidity, permanent fixation, a.s.o. [5].

Taking into account all these aspects, 3 types of wool with different sulphur content were subjected to chemical grafting with acrylic acid, for a subsequent mechano-rheological analysis of the chemically modified fibers, as compared with the reference fibers.

2. Experimental. Wool samples subjected to chemical modifications have been taken from various sheep breeds, such as: Transylvania merino (type 10), Polworth breed (type 11) and Corriedalle breed (type 12), their content of cystinic sulphur – determined by volumetric titration – being presented in Table 1.

Table 1
Sulphur Content of Samples

Breed	Sulphur content, [%]
Transylvania Merino	3.29
Corriedalle	3.94
Polworth	4.04

Potassium persulphate-H_2O system has been employed as redox initiator.

It is generally known that the active species act, too, on the cystinic bridge, according to the following mechanism [5]:

$$R - S - S - R + 2S_2O_8^{2-} \longrightarrow 2RSOSO_3^- + 2SO_4^-$$

$$RSOSO_3^- \longrightarrow RS^{\cdot} + SO_4^-$$

$$SO_4^- + H_2O \longrightarrow HSO_4^- + HO^{\cdot}$$

This is indicative of the fact that persulphate ions penetrate into the fiber, thus forming free radicals, which also favour an internal grafting, besides the surface grafting of the wool fiber.

The grafting mechanism is radicalic, affecting mainly the cystinic bridge and the active species on the fiber surface:

$$R - SH \rightleftharpoons RS^- + H^+$$

$$RS^- + S_2O_8^{2-} \longrightarrow RS^{\cdot} + SO_4^- + SO_4^{2-}$$

$$SO_4^- + H_2O \longrightarrow HO^{\cdot} + HSO_4^-$$

$$SO_4^- + RSH \longrightarrow RS^{\cdot} + HSO_4^-$$

$$HO^{\cdot} + RSH \longrightarrow RS^{\cdot} + H_2O$$

$$RS^{\cdot} + nCH_2 = CHCOOH \longrightarrow RS(CH_2 - CHCOOH)_{n-1}CH_2 - \dot{C}HCOOH$$

$$HO^{\cdot} + nCH_2 = CHCOOH \longrightarrow HO(CH_2 - CHCOOH)_{n-1}CH_2 - \dot{C}HCOOH$$

$$SO_4^- + nCH_2 = CHCOOH \longrightarrow^- SO_4(CH_2 - CHCOOH)_{n-1}CH_2 - \dot{C}HCOOH$$

The grafting degree increases with the monomer concentration, the sulphur content in the fiber and the reaction time, as well (Table 2). With all grafting variants, the reaction is over after 2 hours, as the rate of adsorption and diffusion of the acrylic acid within the fiber, as well as its reactivity towards the macroradicalic substrate are higher than with other vinylic monomers [6].

Analysis of the IR spectra also evidenced a slight condensation of the free aminic groups of keratin:

$$\sim NH_2 + HOOC - CH = CH_2 \longrightarrow \sim NH - CO - CH = CH_2 + H_2O$$

Table 2

Grafted Degree Fonction Sulphur Content

Monomer concentration mol/mol	Sample codification	Sulphur content, %	Grafted degree %
0.1	grafted 1	3.29	28
0.1	grafted 1	4.09	39
0.1	grafted 1	3.94	36
0.2	grafted 2	3.29	50
0.2	grafted 2	4.09	75
0.2	grafted 2	3.94	61
0.3	grafted 3	3.29	62
0.3	grafted 3	4.09	84
0.3	grafted 3	3.94	77

The mechanical characteristics have been determined from the deformation-charge curves recorded on a Fafegraph dynamometer, the following parameters being thus established:

- initial elasticity (E_I, cN/tex);
- limit of elasticity (σ_e, ε_e);
- limit of flow (σ_c, ε_c);
- limit of breaking (σ_r, ε_r);
- specific mechanical work from deformation to breaking, L_{ms}, (cN/tex).

The average values of 20 calculations are listed in Table 3. With increasing the sulphur content in the fiber an increase of the elasticity modulus is to be observed with the reference samples.

The elasticity modulus decreases at the grafted samples, as compared with the reference ones, this tendency being more pronounced with increasing the sulphur content.

The same observation may be made for the indices of resistance: P_e, σ_e, P_c, σ_c, P_r, σ_r and L_{ms}.

All these aspects may be explained by a more rapid scission of the interchain cystinic bridges, comparatively with the recovery of the new reticulation bridges, on new positions, by the action of the acrylic acid.

The rheological characteristics of the reference samples, as well as of the chemically modified ones, have been established through static stresses, with loads of 1.5; 2.5; 3.5; 4.5 cN from the elastic and viscoelastic domains (values established from the charge-deformation curves), representing ratios of the breaking charge.

Deformation modifications under the action of charge have been followed, then, by the release of the fiber from the deformation charge, and its recovery process. The duration of stress (t_1), equal to the duration of recovery, was of 15 min. The number of determinations ranged between 5 and 10, depending on the degree of non-uniformity found.

Starting from the average values of the deformations recorded, both during stress and recovery, the following parameters, have been calculated:

Table 3

Mechanical Characteristics

Sample		Fineness tex	E_I cN/tex	Limit of elasticity			Limit of flow			Limit of breaking			Specific mechanical work, L_{ms}, cN/tex
				P_e cN/fb	σ_e cN/tex	ε_e %	P_c cN/fb	σ_c cN/tex	ε_c %	P_r cN/fb	σ_r cN/tex	ε_r %	
Transylvania Merino	reference	0.460	321.1	4.26	9.26	3.94	7.22	15.69	22.14	9.30	20.21	32.14	4.60
	grafted 1	0.472	311.3	4.15	8.79	4.24	6.73	14.25	23.10	9.11	19.30	34.14	4.71
	grafted 2	0.476	315.2	4.19	8.80	4.12	6.98	14.66	22.88	9.18	19.28	33.80	4.68
	grafted 3	0.482	320.4	4.23	8.77	3.95	7.19	14.91	22.24	9.22	19.12	33.10	4.61
Corriedalle	reference	0.480	363.4	4.75	9.89	4.10	7.30	15.20	21.82	9.84	20.50	30.06	4.73
	grafted 1	0.520	350.5	4.08	7.84	4.62	6.82	13.11	22.62	9.75	18.75	31.20	4.70
	grafted 2	0.530	357.4	4.16	8.11	4.51	6.90	11.32	22.40	9.77	18.43	31.02	4.72
	grafted 3	0.541	362.0	4.22	9.63	4.43	6.94	13.93	22.16	9.81	19.69	30.81	4.77
Polworth	reference	0.502	301.2	5.42	10.84	4.22	7.44	14.88	21.12	10.87	21.74	27.93	4.89
	grafted 1	0.552	321.3	4.99	9.03	4.84	7.02	12.71	22.00	9.60	17.39	28.46	4.86
	grafted 2	0.556	332.4	5.08	9.14	4.75	5.10	12.76	21.60	9.78	17.58	28.20	4.88
	grafted 3	0.562	338.2	5.14	9.13	4.66	7.12	12.74	21.43	9.87	17.56	28.03	4.88

- total deformation, on 15 min stress, (%);
- compounds of elastic recovery (ε, %):
  - instantaneous recovery (ε_1, %);
  - delayed recovery (ε_2, %);
- remanent deformation (ε_3, %);
- degree of elasticity (G_e, %);
- recovery rate (V_r, %/min).

The average values of the Transylvania merino sample are listed in Table 4. Slight decreases of the rheological characteristics have to be observed with the grafted samples, as compared with the reference samples, higher differences being noted with samples having a higher grafting degree.

Table 4
Rheological Characteristics

Sample	P_s cN/fb	$P_s \cdot 100/P_4$ %	Total deformation %	ε_1 %	ε_2 %	ε_3 %	Elasticity degree %	Recovery rate %/min
Transylvania	1.5	16.12	3.0	46.80	27.10	26.10	74.87	4.97
Merino	2.5	26.88	4.7	39.12	26.00	34.88	69.20	4.50
Reference	3.5	37.63	5.3	39.00	23.50	35.80	64.10	4.20
	4.5	48.38	14.2	38.25	22.80	38.95	59.43	3.98
Transylvania	1.5	16.46	3.2	45.21	27.00	27.79	73.45	4.80
Merino	2.5	27.44	5.1	38.10	25.82	36.08	68.10	4.42
Grafted 1	3.5	38.41	5.9	37.80	23.40	38.80	62.92	4.08
	4.5	49.39	14.9	37.20	22.60	40.20	58.12	3.85
Transylvania	1.5	16.33	3.3	44.10	26.30	29.60	72.93	4.72
Merino	2.5	27.23	5.3	37.00	25.12	37.88	67.80	4.30
Grafted 2	3.5	38.12	6.2	36.93	23.07	40.01	62.10	3.93
	4.5	49.01	15.2	36.10	22.14	41.76	57.83	3.71
Transylvania	1.5	16.26	3.5	43.80	25.75	30.45	71.80	4.65
Merino	2.5	27.11	5.5	36.43	24.61	39.96	65.14	4.21
Grafted 3	3.5	37.96	6.4	36.00	23.00	41.00	61.06	3.75
	4.5	48.80	15.8	34.82	21.80	48.38	56.20	3.20

The same evolution of the rheological characteristics has been found for the other grafted samples of wool, too.

The fibers fineness has been established on measuring the fiber diameter on a Lanameter, followed by determination of the fibers density.

The actions of the acrylic acid on the wool fiber is more complex. Thus, the fact has been evidenced that, as compared with mineral acids, at the same pH values, wool swelling is more pronounced in organic acids [7]. The higher swelling degree may be explained by the volume of the acrylic acid molecule as well as by the hydrophobic fiber-acid interactions. The hydrophobic segments of keratine molecular chain get disorganized along the hydrophobic parts of the organic acid.

3. Conclusions Wool grafting with acrylic acid as a redox-initiated process is very complex, being mainly influenced by the monomer concentration, its diffusion, both by temperature and fiber sulphur content.

Unlike the mechanical and rheological characteristics obtained for wool fibers grafted with other vinylic monomers [8], those recorded in processes of grafting with acrylic acid show a lower diminishing of such characteristics.

The grafting degree increases with increasing the fiber sulphur content, yet the mechanical characteristics are not reduced proportionally to the grafting degree, as due to the compensatory formation of some new interchain bonds by condensation of the free COOH groups from the ends of the polyacrylic acid grafted on the fiber with keratin NH_2 groups.

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MODIFICAREA PRIN GREFARE INIŢIATĂ REDOX A UNOR TIPURI DE FIBRE DE LÂNĂ INDIGENĂ

(Rezumat)

Sunt abordate trei sorturi de lână indigenă, cu conţinut diferit de sulf, care au fost grefate, prin iniţiere redox, cu acid acrilic.

S-a constatat o grefare superficială şi internă a fibrei.

Au fost determinaţi parametri fizici, mecanici şi reologici ai fibrelor modificate şi ai fibrelor martor.

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WOOL'S GRAFTING THROUGH INITIATION WITH UV RADIATIONS

II. ESTABLISHMENT OF THE OPTIMUM CONDITIONS FOR GRAFTING WITH HYDROXYALKYL-ACRYLIC MONOMERS

BY
ADRIANA GRECU, V. BLAŞCU,
AURELIA GRIGORIU and ELENA COSTEA

1. Introduction. The reactions of wool fibers' grafted copolymerization, some of their properties – such as resistance to warm water, to alkalies, to light, elastic recovery, permanent fixation, surface aspect – may be improved, alonguith conferring them some new properties, such as electrical conductivity [1],...,[5].

All these characteristics may be attained through diversification of both monomers and grafting techniques. In this respect, a previous of ours paper [6] had been devoted to grafting of alkyl-acrylates on wool, while the present study aims at the optimization of the grafting conditions for acrylated hydroxyalkyl products.

2. Experimental. UV-initiated graftings have been applied to semifine Romanian wool fibers of the 22 type, with three hydroxyalkyl-acrylic monomers of a homologous series (Table 1). The working method has been discuted in §2 of previous paper [6].

Table 1

Acrylic Hydroxyalkyl Monomers Employed in Reactions of Wool's Grafting

Monomer	Chemical formula	Symbol
2-Hydroxyethyl acrylate	$CH_2 = CH$ $\vert$ $COO-CH_2-CH_2-OH$	HEA
3-Hydroxypropyl acrylate	$CH_2 = CH$ $\vert$ $COO-CH_2-CH_2-CH_2-OH$	HPA
4-Hydroxybutyl acrylate	$CH_2 = CH$ $\vert$ $COO-CH_2-CH_2-CH_2-CH_2-OH$	HBA

3. Results and Discussion. The optimum parameters for the grafting reaction have been established with a centrated, rotatable, composite second-oder experimental program with 3 independent variables [7].

The values of the reaction's parameters (independent variables) have been coded as presented in Table 2. As response functions (Y), the four functions discussed in the previous paper have been selected [6].

Table 2

Real and Coded Values of the Parameters of the Wool-Hydroxyalkyl Acrylic Monomer Grafting Reaction

Real variable	Coded variable				
	−1.682	−1	0	1	1.682
x_1, mL monomer	0.5	0.8	1.25	1.7	2
x_2, minutes	13	20	30	40	47
x_3, g photosensitizer	0.0800	0.1043	0.1399	0.1755	0.2000

The experimental program, the experimental and calculated values obtained are listed in Tables 3,...,5, while the values of Y have been calculated as in the above mentioned study and they are following:

for hydroxyethyl acrylate:

$$G,\ [\%]\quad Y = 27.22 + 4.863x_1 + 3.91x_2 + 2.768x_3 - 2.911x_1^2 - 1.456x_2^2 - 0.617x_3^2 + 0.692x_1x_2 + 0.74x_1x_3 + 0.475x_2x_3$$

$$\overline{d},\ [\mu m]\quad Y = 26.102 + 0.0071x_1 + 0.016x_2 + 0.747x_3 - 0.5277_1^2 - 0.626x_2^2 - 0.416x_3^2 + 0.261x_1x_2 + 0.232x_1x_3 - 0.0198x_2x_3$$

$$\overline{P}_r,\ [g/fb]\quad Y = 17.7134 + 1.6236x_1 + 1.6375x_2 + 1.3305x_3 - 0.5277x_1^2 - 0.1192x_2^2 - 0.0841x_3^2 + 0.7625x_1x_2 + 0.7275x_1x_3 + 0.425x_2x_3$$

$$\overline{\varepsilon}_r,\ [\%]\quad Y = 26.597 + 0.6883x_1 + 0.5822x_2 + 0.7401x_3 - 0.3211x_1^2 - 0.2769x_2^2 - 0.1425x_3^2 + 0.3912x_1x_2 + 0.4137x_1x_3 + 0.3637x_2x_3$$

for hydroxypropyl acrylate:

$$G,\ [\%]\quad Y = 29.934 + 4.728x_1 + 2.766x_2 + 2.794x_3 - 3.026x_1^2 - 1.362x_2^2 - 0.538x_3^2 + 0.602x_1x_2 + 0.699x_1x_3 + 0.357x_2x_3$$

$$\overline{d},\ [\mu m]\quad Y = 27.413 + 0.0052x_1 + 0.018x_2 - 0.0055x_3 - 1.205x_1^2 - 0.515x_2^2 - 0.263x_3^2 + 0.046x_1x_2 + 0.0312x_1x_3 + 0.310x_2x_3$$

$$\overline{P}_r,\ [g/fb]\quad Y = 23.404 + 1.774x_1 + 1.266x_2 + 0.907x_3 - 1.205x_1^2 - 0.618x_2^2 - 0.178x_3^2 + 0.121x_1x_2 + 0.0217x_1x_3 + 0.0411x_2x_3$$

$$\overline{\varepsilon}_r,\ [\%]\quad Y = 28.703 + 0.708x_1 + 0.6029x_2 + 0.2806x_3 - 0.493x_1^2 - 0.2826x_2^2 - 0.1747x_3^2 + 0.1924x_1x_2 + 0.022x_1x_3 + 0.0475x_2x_3$$

for hydroxybutyl acrylate:

$$G,\ [\%]\quad Y = 30.521 + 4.755x_1 + 3.743x_2 + 2.822x_3 - 3.028x_1^2 - 1.378x_2^2 - 0.612x_3^2 + 0.658x_1x_2 + 0.6612x_1x_3 + 0.363x_2x_3$$

$$\overline{d},\ [\mu m]\quad Y = 30.452 + 1.528x_1 + 1.089x_2 + 0.865x_3 - 0.767x_1^2 - 0.569x_2^2 - 0.398x_3^2 + 0.271x_1x_2 + 0.253x_1x_3 - 0.0288x_2x_3$$

$$\overline{P}_r,\ [g/fb]\quad Y = 24.077 + 1.719x_1 + 0.8499x_3 - 1.261x_1^2 + 1.297x_2 - 0.5484x_2^2 - 0.3132x_3^2 + 0.0212x_1x_2 + 0.0512x_1x_3 - 0.0188x_2x_3$$

$$\overline{\varepsilon}_r,\ [\%]\quad Y = 28.9605 + 0.702x_1 + 0.5248x_2 + 0.3123x_3 - 0.396x_1^2 - 0.3346x_2^2 - 0.3099x_3^2 + 0.203x_1x_2 - 0.0338x_1x_3 - 0.0034x_2x_3$$

Table 3

Experimental Schedule and Obtained Results for Hydroxyethyl Acrylate

Nr.	Coded variable			G, [%]		$\overline{d}$, [μm]		$\overline{P}_r$, [g/fb]		$\overline{\varepsilon}_r$, [%]	
	x_1	x_2	x_3	real	calculated	real	calculated	real	calculated	real	calculated
1	−1	−1	−1	13.56	14.26	24.81	25.16	16.91	17.21	25.40	24.19
2	1	−1	−1	17.70	18.24	26.40	27.70	18.80	18.33	27.70	27.80
3	−1	1	−1	17.04	16.94	25.77	26.23	18.82	19.41	26.72	28.84
4	1	1	−1	30.17	31.68	29.58	29.98	23.33	24.18	28.51	29.16
5	−1	−1	1	16.11	17.20	25.61	27.61	18.00	18.32	26.21	27.14
6	1	−1	1	29.26	30.23	29.40	28.56	22.62	24.16	27.30	28.20
7	−1	1	1	27.37	26.88	27.82	29.14	23.37	25.03	27.22	28.00
8	1	1	1	36.78	35.30	31.32	32.46	24.50	26.10	28.94	29.64
9	−1.682	0	0	15.91	17.06	25.77	26.82	17.32	18.11	26.12	28.40
10	1.682	0	0	29.80	28.42	30.34	31.10	23.47	22.33	29.38	31.28
11	0	−1.682	0	23.11	24.18	26.50	28.46	20.98	21.18	26.86	28.11
12	0	1.682	0	32.83	31.76	30.56	31.28	23.91	25.16	28.04	29.85
13	0	0	−1.682	28.00	29.18	27.71	27.02	22.50	23.60	26.96	28.13
14	0	0	1.682	32.35	31.17	30.33	29.23	24.62	23.80	28.02	29.11
15	0	0	0	29.80	29.04	29.61	28.77	23.23	22.82	28.24	28.92
16	0	0	0	29.88	29.04	29.64	28.77	23.28	22.82	28.25	28.92
17	0	0	0	28.83	29.04	29.62	28.77	23.25	22.82	28.24	28.92
18	0	0	0	29.78	29.04	29.57	28.77	23.19	22.82	28.18	28.92
19	0	0	0	29.85	29.04	29.63	28.77	23.27	22.82	28.23	28.92
20	0	0	0	28.90	29.04	29.67	28.77	23.26	22.82	28.27	28.92

As to the photosensitizer employed, the part it plays in the photopolymerization reactions is that of the "messenger" of the UV radiating energy to the reactants, the literature in the field making mention of the high efficiency of benzophenone and riboflavine in reactions of textile fibers' grafting [8],...,[10]. When

Table 4

Experimental Schedule and Obtained Results for Hydroxypropyl Acrylate

Nr.	Coded variable			G, [%]		$\bar{d}$, [μm]		$\bar{P}_r$, [g/fb]		$\bar{\varepsilon}_r$, [%]	
	x_1	x_2	x_3	real	calculated	real	calculated	real	calculated	real	calculated
1	−1	−1	−1	10.80	12.60	23.90	24.81	13.93	14.47	24.72	25.01
2	1	−1	−1	14.86	19.46	24.87	26.02	14.12	14.74	24.48	24.78
3	−1	1	−1	14.53	18.09	25.13	27.16	14.60	15.37	24.02	24.66
4	1	1	−1	27.46	27.71	28.81	28.61	17.81	18.69	25.27	26.00
5	−1	−1	1	13.00	15.70	24.53	26.12	14.24	14.83	24.96	24.94
6	1	−1	1	26.13	25.53	28.01	28.82	17.31	18.00	26.30	26.36
7	−1	1	1	24.73	23.09	25.14	27.16	16.58	17.43	25.64	26.04
8	1	1	1	34.53	35.68	29.62	31.08	22.73	23.65	28.62	29.03
9	−1.682	0	0	13.20	10.80	23.94	24.60	14.42	13.48	24.98	24.53
10	1.682	0	0	28.95	27.16	28.16	28.97	20.10	18.95	27.40	26.84
11	0	−1.682	0	20.15	16.52	24.63	26.38	15.37	14.62	24.87	24.83
12	0	1.682	0	30.23	29.68	29.04	31.00	21.46	20.13	27.76	26.79
13	0	0	−1.682	25.46	20.81	25.78	27.32	16.68	15.71	25.78	24.94
14	0	0	1.682	29.77	30.13	28.64	28.02	21.30	20.18	27.61	27.43
15	0	0	0	27.12	27.22	28.97	28.25	17.74	17.71	26.66	26.59
16	0	0	0	27.09	27.22	28.93	28.25	17.68	17.71	26.57	26.59
17	0	0	0	27.14	27.22	28.89	28.25	17.62	17.71	26.52	26.59
18	0	0	0	27.10	27.22	28.96	28.25	17.64	17.71	26.55	26.59
19	0	0	0	27.08	27.22	28.91	28.25	17.67	17.71	26.56	26.59
20	0	0	0	27.10	27.22	28.87	28.25	17.60	17.71	26.59	26.59

testing the efficiency of benzophenone and benzyl-dimethyl ketal, the observation was made that, in our reaction systems, the highest efficiency was shown by benzyl-dimethyl ketal (Irgacure 651, Ciba Geigy). Also, a superphotosensitizer (the Michler's ketone) has been associated to the reaction system, which further increased the efficiency of grafted photocopolymerization of wool fibers. For hindering the action of caloric radiations, inducing the monomers thermic polymerization during grafting, a highly efficient thermal inhibitor – i.e., 4-methoxyphenol – has been employed.

4. Conclusion. A comparative analysis of the behaviour evidenced by the 3 hydroxyalkyl acrylic monomers employed in the UV-photoinitiated grafting of semifine Romanian wool evidences a decrease of the grafting degree through increase of the carbohydrated chain from the homologous series, as a result of the steric hindrances. The same phenomenon of steric hindrance has been observed, as well, during grafted copolymerization of the wool fibers, initiated with gamma radiations, with methyl and, respectively, ethyl metacrylate [11], and also with alkyl acrylic monomers from the homologous series [6].

A comparison of the acrylic hydroxyalkyl monomers' reactivity with that of the acrylic alkyl ones permits the following observations:

Table 5

Experimental Schedule and Obtained Results for Hydroxybutyl Acrylate

Nr.	Coded variable			G, [%]		$\bar{d}$, [μm]		$\bar{P}_r$, [g/fb]		$\bar{\varepsilon}_r$, [%]	
	x_1	x_2	x_3	real	calcu-lated	real	calcu-lated	real	calcu-lated	real	calcu-lated
1	-1	-1	-1	10.20	12.32	23.10	20.45	13.60	12.40	24.13	25.06
2	1	-1	-1	13.98	17.43	24.12	23.18	14.02	13.20	24.06	23.90
3	-1	1	-1	14.03	17.84	24.62	23.41	14.31	12.10	24.35	23.60
4	1	1	-1	26.24	26.52	28.20	26.71	17.18	16.48	24.90	26.07
5	-1	-1	1	12.45	15.76	23.74	22.20	13.90	11.98	24.08	23.63
6	1	-1	1	25.71	24.22	26.17	24.51	16.77	14.65	25.47	26.32
7	-1	1	1	24.20	23.16	25.06	23.68	16.23	14.20	24.97	22.83
8	1	1	1	33.81	34.67	30.07	28.97	22.14	18.77	27.88	28.61
9	-1.682	0	0	12.66	10.11	23.70	22.17	13.91	12.50	24.10	25.20
10	1.682	0	0	28.21	27.02	28.13	26.56	19.40	16.62	26.74	25.17
11	0	-1.682	0	19.50	15.30	24.22	23.48	14.84	13.48	24.20	23.77
12	0	1.682	0	29.72	29.08	29.36	28.63	21.04	20.14	27.10	28.40
13	0	0	-1.682	24.84	21.06	25.28	23.20	16.11	14.17	25.14	26.39
14	0	0	1.682	29.03	30.16	28.82	27.62	20.77	18.18	26.96	25.56
15	0	0	0	26.55	26.71	28.75	28.12	17.10	15.21	26.01	24.91
16	0	0	0	26.46	26.71	28.63	28.12	17.02	15.21	25.94	24.91
17	0	0	0	26.61	26.71	28.70	28.12	17.17	15.21	25.89	24.91
18	0	0	0	26.59	26.71	28.67	28.12	17.08	15.21	25.90	24.91
19	0	0	0	26.49	26.71	27.72	28.12	17.11	15.21	26.04	24.91
20	0	0	0	26.53	26.71	28.66	28.12	17.15	15.21	25.97	24.91

– the hydroxyethyl acrylate's reactivity is higher than that of butyl acrylate's and lower than that of ethyl and propyl acrylate;

– the reactivity of hydroxypropyl acrylate and hydroxybutyl acrylate is lower than that of all other alkyl acrylated monomers taken into study, the differences observed being induced by the steric hindrances caused both by the volume of carbohydrated chain and by the presence of the hydroxylic groups.

The grafted fibers' diameter increases with the increase of the grafting degree, remaining nevertheless within quite normal limits (up to 20%, for a grafting degree of 27%), which has no consequences upon the fiber's subsequent processing.

The resistance parameters of the grafted fibers increase, comparatively with those of the reference fibers, as a result of a minimum destruction of the fiber's supermolecular structure and, probably, of an additional reticulation in the fiber, induced by the grafted polymer. The same phenomenon was observed in processes of wool's grafting with alkyl acrylic monomers [6]. Nevertheless, the literature of the field presents – in the case of grafting processes on wool through either redox initiation or gamma radiations (CO^{60}) – a reduction of the resistance parameters, as a result of the destruction processes occurring within the fiber.

All these experiments are still to be developed in further studies, that will ana-

lyze the influence of the monomer's nature upon the physical, mechano-rheological and chemical properties of the modified wool fibers, in parallels with suggesting some new reaction mechanisms. Also, by the application of different methods, grafting's authenticity will be demonstrated, alongwith the process' topochemistry and recommendation of several applicative directions for the grafted fibers.

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GREFAREA LÂNII PRIN INIŢIERE CU RADIAŢII UV

II. Stabilirea condiţiilor optime la grefarea cu monomeri hidroxialchil acrilici

(Rezumat)

Se studiază grefarea pe lână semifină românească a 3 monomeri din serie omoloagă (acrilat de hidroxietil, de hidroxipropil şi de hidroxibutil) prin iniţiere neconvenţională - radiaţii UV.

Au fost stabilite, pe baza unui program experimental cu 3 variabile, condiţiile optime de grefare. Pentru fiecare monomer s-au stabilit câte 4 funcţii de răspuns (Y).

Se compară reactivitatea, în grefarea lânii, a monomerilor hidroxialchil acrilici cu cea a monomerilor alchil acrilici.

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Secţia VIII
TEXTILE. PIELĂRIE

EIGENSCHAFTSVERÄNDERUNGEN DER FÄDEN AUS FLACHS ODER VOM FLACHSTYP DURCH VERDOPPELUNG DES VORGARNS BEIM SPINNEN

VON
CARMEN CUZIC-ZVONARU

1. Einführung. Das natürliche ungleichmässige Aussehen der Flachsfäden spielt eine bedeutende Rolle in der Ästhetik der hergestellten Erzeugnisse. Der sogenannte „Flachs-Effekt" wird bei den meisten Webwaren gebilligt (ja, er wird bei der Kleidung sogar verlangt), doch kann seine Anwesenheit auch stören, und zwar im Falle der Erzeughisse, bei denen ein möglichst gleichmässig feiner Faden gewünscht wird (wie z.B. beim Nähzwirn). Das bedeutet, dass in Anhängigkeit vom Zweck, die Ungleichmässigkeit der Fäden vom Flachstyp geduldet werden kann, jedoch in einem gewissen Gleichgewicht zwischen der wirtschaftlichen, von den Bearbeitungsbedingungen beeinflussten Seite und der ästhetischen, von den auferlegten Bedingungen des Verbrauchers geprägten Seite.

Von dieser Tatsache ausgehend, werden im folgenden neue Kategorien von Fäden aus flachsartigen Fasern vorgestellt, die in nassem Zustand aus doppeltem Vorgarn gesponnen wurden. Im Verfleich zu den normalen Fäden (von gleicher Feinheit) weisen diese Veränderungen ihrer Charakteristiken auf, so dass sich ihr Anwendungsgebiet erweitern konnte, aber auch in der Spinnerei oder Weberei mit klar verbesserten Produktionsindexen gearbeitet wurde [1], [2].

2. Experimenteller Teil. Um einen allgemeinen Überblick über die Forschungen zu haben, wurden die drei üblichen, in der Abteilung schon zur Tradition gewordenen Gemische, u.zw. 67% Flachs/33% PET, 50% Flachs/50% PET und 33% Flachs/67% PET, verfolgt, die man als repräsentativ auch für andere Kategorien von chemischen chemischen Fasern ansieht, die neben dem Flachs an der Fabrikation teilnehmen könnten [3], [4].

Die Flachsriste und die Polyesterfasern, nach dem klassischen Kammverfahren bearbeitet, durchliefen die gleiche Technologie bis zur Nassspinnmaschine. Vom Fleier lieferte man ein Vorgarn von Nm 2,6. Wegen der Verdoppelung des Vorgarns wurde auf der Nassspinnmaschine mit zwei Längen gearbeitet ($L = 7,6$ und $L = 15,2$), wobei ein Faden mit einer Feinheit von Nm 20 erzielt wurde, eine Feinheit, die als repräsentativ im Bereich Flachs-Hanf angesehen wird. Man stellte 24 Fadenvarianten her, durch Veränderung der Wassertemperatur auf T (20, 30,

40 und 50)°C. Das Wasser wurde zur Immersion des Faserstoffs gebraucht.

Man analysierte: den Einfluss der Verdoppelung des Vorgarns auf die Feinheitsgleichmässigkeit (für durchschnittliche Abschnitte); es wurden über 6000 Einzelproben testiert, indem auf dem Dynamometer Zwigg die Bruchlast und die Bruchstreckung bestimmt wurden; zum Vergleich zeichnete man die Ebene der Risse auf.

Die Daten bezüglich Zugfestigkeit der Fäden, durch die durchschnittliche Tenazität τ widerspiegelt (bei $D = 1$, τ_{D_1} und bei $D = 2$, τ_{D_2}), sowie auch durch die durchschnittliche Bruchstreckung ε (bei $D = 1$, ε_{D_1} und bei $D = 2$, ε_{D_2}), wurden analytisch auf dem Programm PROUNFAC 1 aus der Bibliothek STATEX verarbeitet, wobei man die Regressionsgleichungen (1)...(12) aus den Tabellen 1, 2 und 3 erheilt. Diese können zusammen mit den Variationskurven (1)...(12) eine Datensammlung bilden, die Prüfungen, Kontrollen und operative Eingriffe ermöglichen, wenn man höhere Ansprüche an die Qualität der Fäden stellt.

Tabelle 1

Gemisch: 67% Flachs + 33% PET

T, [°C]		20	30	40	50
τ	$D = 1$	13,46	14,05	14,59	13,68
cN/tex	$D = 2$	15,90	16,20	16,90	15,89
ε	$D = 1$	6,20	6,25	6,32	5,96
%	$D = 2$	2,74	2,86	3,16	2,78

$$\tau_{D_1} = 9,4 + 0,274T - 0,02T^2 \quad (1)$$

$$\tau_{D_2} = 12,3 + 0,235T - 0,004T^2 \quad (2)$$

$$\varepsilon_{D_1} = 5,282 + 0,065T - 0,02T^2 \quad (3)$$

$$\varepsilon_{D_2} = 1,363 + 0,910T - 0,02T^2 \quad (4)$$

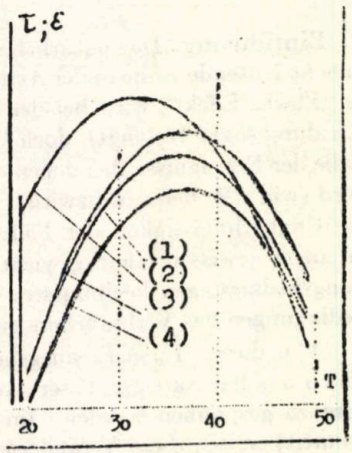


Tabelle 2

Gemisch: 50% Flachs + 50% PET

T, [°C]		20	30	40	50
τ	$D = 1$	13,30	14,40	14,63	14,11
cN/tex	$D = 2$	17,02	17,66	18,31	16,54
ε	$D = 1$	10,06	10,28	10,68	8,98
%	$D = 2$	4,06	4,20	4,78	4,12

$$\tau_{D_1} = 8,704 + 0,311T - 0,005T^2 \quad (5)$$

$$\tau_{D_2} = 11,031 + 0,413T - 0,007T^2 \quad (6)$$

$$\varepsilon_{D_1} = 5,714 + 0,307T - 0,005T^2 \quad (7)$$

$$\varepsilon_{D_2} = 1,824 + 0,147T - 0,003T^2 \quad (8)$$

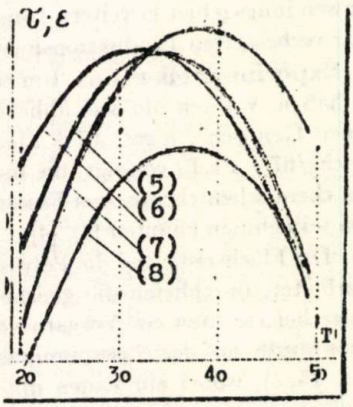
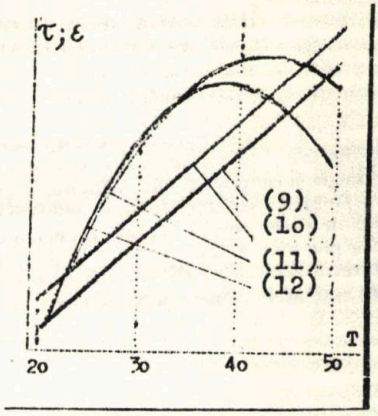


Tabelle 3

Gemisch: 33% Flachs + 67% PET

T, [°C]		20	30	40	50
τ	$D = 1$	16,10	16,32	18,74	18,46
cN/tex	$D = 2$	19,42	20,21	22,34	21,75
ε	$D = 1$	12,04	13,16	14,11	13,10
%	$D = 2$	6,66	7,61	8,08	7,94



$$\tau_{D_1} = 14,758 + 0,736T \quad (9)$$

$$\tau_{D_2} = 17,738 + 0,916T \quad (10)$$

$$\varepsilon_{D_1} = 5,828 + 0,412T - 0,006T^2 \quad (11)$$

$$\varepsilon_{D_2} = 1,363 + 0,910T - 0,003T^2 \quad (12)$$

3. Schlußfolgerungen. Es ergeben sich folgende Schlußfolgerungen aus den Veränderungen der Charakteristiken der erhaltenen Fäden, während dem Nassspinen, *nur* durch die einfache Verdoppelung des Vorgarns im Speisungsgestell:

- Anwachsen der Gleichmässigkeit der Feinheit der Fäden, unabhängig vom Gemisch, um wenigstens 10%;

- Anwachsen der Tenazität der Fäden, unabhängig vom Gemisch, um mindestens 15%;

- Verringerung der Bruchstrecke um wenigstens 42%;

- Verringerung der Risszahl um mindestens 7%.

Die vorgeschlagene Lösung ist von grossem Nutzen für den Fadenhersteller sowie auch für diejenigen, die sich mit der Fadenverarbeitung beschäftigen (vor allem in der Weberei). Man kann schnell und einfach eingreifen, wenn nichtentsprechende Productivitäten wegen eines ungeeigneten Rohstoffes auftreten. Solche Fälle treffen wir häufig im Bereich Flachs-Hanf an, wenn im Gemisch der Anteil der Naturfaser erhöht wird.

Eingegangen am 15. Juni 1994

Technische Universität „Gh. Asachi", Jassy, Lehrstuhl für Spinnerei und Weberei

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ÎMBUNĂTĂŢIREA PROPRIETĂŢILOR FIRELOR DE IN ŞI TIP IN PRIN DUBLAREA SEMITORTULUI LA FILARE

(Rezumat)

În tehnologiile moderne de filare, dublarea semitortului în rastelul maşinii de filat constituie una din cele mai controversate probleme deoarece nu se defineşte incidenţa dintre costurile de producţie şi calitatea firelor obţinute.

Dublarea semitortului în cazul filării în *stare udă* a firelor subţiri de in aduce corecţii în faza finală de prelucrare în filatură, influenţând asupra creşterii valorice a parametrilor calitativi ai firelor pieptănate: uniformitatea de fineţe pe porţiuni medii se îmbunătăţeşte; tenacitatea noilor fire creşte cu până la 32%. Metoda deschide perspectiva lărgirii sortimentului de articole destinate pieţii spre acele domenii unde se cere o stabilitate accentuată a formei.

BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Tomul XLI (XLV), Fasc. 1–2, 1995
Secţia VIII
TEXTILE. PIELĂRIE

AN ALGORYTHM FOR THE CALCULATION OF WOVENS' COMPACTNESS DEGREE

I. THE COMPACTNESS DEGREE FOR SIMPLE WOVENS

BY

DANIEL CHINCIU, GABRIEL CORNELIU CHINCIU and IRINA CRISTIAN

1. Introduction. The degree of compactness represents the percent expression of the way in which the filling capacity of a woven material is occupied with yarns, its maximum value being 100%. The closer to the 100% is a system's compactness degree, the closer to the maximum value is the technological thickness of the fibers from the system. Exceeding the maximum value of the thickness degree assumes exceeding of the maximum technological thickness values, which is manifested in fibres' crushing and overstressing during compression and strain efforts. This phenomenon induces an abnormal increase of the yarns' breaking, which influences negatively the machine's yield and the woven's quality. The compactness degree is the most important parameter and, at the same time, the most complex index in the appreciation of a woven's characteristics [1], [2].

The compactness degree of a woven material is defined by the percent ratio between real (P) and maximum thickness ($P_{\max}$) of the yarns in the system considered, being calculated with the following realtions:

$$Ku = \frac{Pu}{Pu_{\max}} \cdot 100, \tag{1}$$

$$Kb = \frac{Pb}{Pb_{\max}} \cdot 100, \tag{2}$$

while, for the woven material:

$$Kt = \frac{Ku + Kb}{2}. \tag{3}$$

2. Calculation of the Compactness Degree as a Function of the Yarns' Fineness, Expressed by the Diameter. The maximum thickness values $Pu_{\max}$ and $Pb_{\max}$ from relations (1) and (2) may be determined from the number of weave repeat n_{Ru} and n_{Rb}, that may be found in 100 mm of woven material, which could be determined as follows:

a. *as a function of the number of yarns from a Ru and Rb weave repeat:*

$$n_{Ru} = \frac{Pu_{\max}}{Ru} \quad \text{and} \quad n_{Rb} = \frac{Pb_{\max}}{Rb}. \tag{4}$$

b. *as a function of a L_{Ru} and L_{Rb} weave repeat:*

$$n_{Ru} = \frac{100}{L_{Ru}} \quad \text{and} \quad n_{Rb} = \frac{100}{L_{Rb}}. \tag{5}$$

Equalization of the (4) and (5) values leads to:

$$Pu_{\max} = \frac{Ru}{L_{Ru}} \cdot 100 \quad \text{and} \quad Pb_{\max} = \frac{Rb}{L_{Rb}} \cdot 100. \tag{6}$$

Substituing the values from (6) into (1) and (2), respectively, there results that the compactness degree may be calculated with the relation:

$$Ku = \frac{Pu \cdot L_{Ru}}{Ru}, \tag{7}$$

$$Kb = \frac{Pb \cdot L_{Rb}}{Rb}. \tag{8}$$

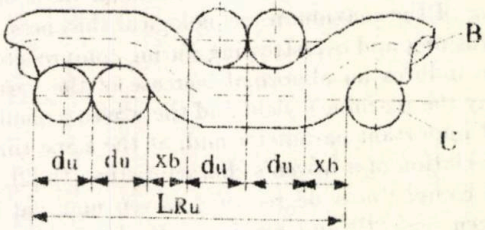


Fig. 1.– Cross section in a woven fabric with minimum geometric thickness.

On considering the longitudinal section of a woven material with maximum technological thickness and $D\frac{2}{2}$ stitch, or any other stitch, plain weave excepted, the lenght of the weave repeat, (Fig.1), for the L_{Ru} warp system becomes:

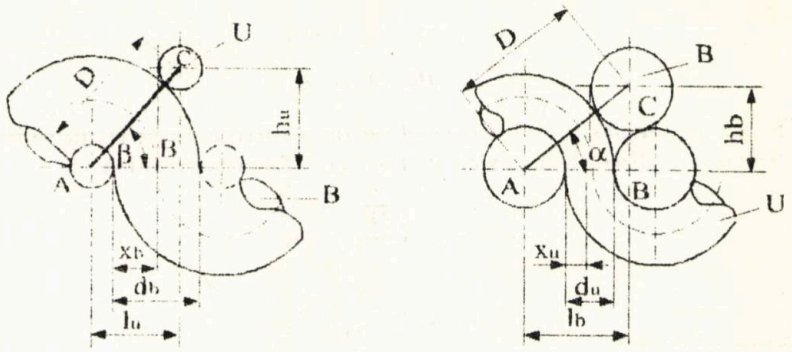
$$L_{Ru} = d_u \cdot Ru + x_b \cdot t_b. \tag{9}$$

Similarly for the weft, one may have:

$$L_{Rb} = d_b \cdot Rb + x_u \cdot t_u, \tag{10}$$

where x_b, x_u are the minimum distance between the two consecutive warps and, respectively, weft yarns through which a yarn from the opposite system is passed, measured horizontally.

Fig.2 shows that:



a b.

Fig. 2.– Sections in a woven element with minimum geometrical thickness; *a* – cross section; *b* – longitudinal section.

$$x_u = l_u - d_u \tag{11}$$

and

$$x_b = l_b - d_b, \tag{12}$$

while, from the ABC triangle, one may obtain:

$$l_u = D \cdot \cos\beta, \tag{13}$$

$$l_b = D \cdot \cos\alpha. \tag{14}$$

Substituting the l_u and l_b values from (13) and (14) in (12) and then in (9) and (10), there results that:

$$L_{Ru} = d_u \cdot Ru + (D \cdot \cos\beta - d_u)t_b, \tag{15}$$

$$L_{Rb} = d_b \cdot Rb + (D \cdot \cos\alpha - d_b)t_u. \tag{16}$$

After substituting the values from (15) and (16) in (7) and (8) the calculation relations for the filling degree are obtained:

a. *Woven fabrics with stitchs (other than plain weave) for which:* $Ru \neq t_u$ *and* $Rb \neq t_b$ *or/and* $Ru \neq Rb$ *and* $t_u \neq t_b$*:*

$$Ku = \frac{Pu[d_u Ru + (D\cos\beta - d_u)t_b]}{Ru}, \tag{17}$$

$$Kb = \frac{Pb[d_b \cdot Rb + (D \cdot \cos\alpha - d_b)t_u]}{Rb}. \tag{18}$$

b. *Woven fabrics with plain weave (for which* $Ru = Rb = t_u = t_b$*):*

$$Ku = Pu \cdot D \cdot \cos\beta, \tag{19}$$

$$Kb = Pb \cdot D \cdot \cos\alpha. \tag{20}$$

The waving angles α and β depend on the structure phase (i) in which the woven fabric is realized, being calculated with the following relations:

$$\cos\beta_i = \frac{\sqrt{D^2 - h_{ui}^2}}{D}, \tag{21}$$

$$\cos\alpha_i = \frac{\sqrt{D^2 - h_{bi}^2}}{D}, \tag{22}$$

where: Pu, Pb represent thickness of the warp and, respectively, weft system in yarns/10 cm; du, db – diameters of the warp and weft yarns, in mm; D – sum of the $(d_u + d_b)$ diameters, in mm; t_u, t_b – number of passings of the warp and weft fibers in the Rb limits, and the reciprocal; $\cos\alpha$, $\cos\beta$ – the waving angles of the warp and weft system, respectively; h_{ui} and h_{bi} – wave heights, calculated either from the values of the phase intervales (h) or by the thickness method; l_u, l_b – geometrical thickness of the warp and weft system, respectively.

3. Algorithm for the Calculation of the Compactness Degree as a Function of the Fibers Fineness, Expressed as Tex. On passing from the fineness of fibers expressed by the diameter to that expressed by Tex, relations (17) and (18) become:

a. *Woven fabrics with stitchs in which* $Ru \neq t_u$ *and* $Rb \neq t_b$ *or/and* $Ru \neq Rb$, $t_u \neq t_b$:

$$Ku = \frac{Pu[Ru\sqrt{Tu} + (\sqrt{Tu} + \sqrt{Tb})t_b \cos\beta - t_b\sqrt{Tu}]A}{Ru}, \tag{23}$$

$$Kb = \frac{Pb[Rb\sqrt{Tb} + (\sqrt{Tu} + \sqrt{Tb})t_u \cos\alpha - t_u\sqrt{Tb}]A}{Rb}. \tag{24}$$

b. *Woven fabrics with plain weave:*

$$Ku = A \cdot Pu(\sqrt{Tu} + \sqrt{Tb})\cos\beta, \tag{25}$$

$$Kb = A \cdot Pb(\sqrt{Tu} + \sqrt{Tb})\cos\alpha. \tag{26}$$

4. Algorithm for the Calculation of the Compactness Degree as a Function of Average Floating. Average floating represents the R/t ratio, where R expresses the weave repeat, and t the number of passings of the fibers in a system through the yarns of the opposite system, within a weave repeat. Average floating on systems of yarns is:

$$Fu = \frac{Rb}{t_u}, \tag{27}$$

$$Fb = \frac{Ru}{t_b}. \tag{28}$$

4.1. Calculation of the Compactness Degree by the Diameter Method.

a. *Woven fabrics with stitchs characterized by:* $Ru \neq Rb$ *and* $t_u \neq t_b$.

The compactiness degree as a functions of average floating may be calculated from the relation obtained by introducing the values from (27) and (28) in (17) and (18), the result being the following:

$$Ku = Pu\left[d_u + \frac{1}{Fb}(D \cdot \cos\beta - d_u)\right] \tag{29}$$

and

$$Kb = Pb\left[d_b + \frac{1}{Fu}(D \cdot \cos\alpha - d_b)\right]. \tag{30}$$

b. *Woven fabrics with the stitchs characterized by:* $Ru = Rb = R$ *and* $t_u = t_b = t$.

For woven materials with both fundamental and derived weaves, meeting such requirements, the compactness degree as a function of average floating is calculated with the relation:

$$Ku = Pu\left[d_u + \frac{1}{F}(D \cdot \cos\beta - d_u)\right], \tag{31}$$

$$Kb = Pb\left[d_b + \frac{1}{F}(D \cdot \cos\alpha - d_b)\right]. \tag{32}$$

4.2. Calculation of the Compactness Degree by the Method of Tex Fineness

a. *Wovens with stitchs characterized by:* $Ru \neq Rb$ *and* $t_u \neq t_b$.

$$Ku = \frac{Pu\sqrt{Tu}}{Fb}\left(Fb - 1 + \frac{\sqrt{Tu} + \sqrt{Tb}}{\sqrt{Tb}}\cos\beta\right)A, \tag{33}$$

$$Kb = \frac{Pb\sqrt{Tb}}{Fu}\left(Fu - 1 + \frac{\sqrt{Tu} + \sqrt{Tb}}{\sqrt{Tu}}\cos\alpha\right)A. \tag{34}$$

b. *Wovens with stitchs characterized by:* $Ru = Rb = R$ *and* $t_u = t_b = t$.

$$Ku = \frac{Pu\sqrt{Tu}}{F}\left(F - 1 + \frac{\sqrt{Tu} + \sqrt{Tb}}{\sqrt{Tb}}\cos\beta\right)A, \tag{35}$$

$$Kb = \frac{Pb\sqrt{Tb}}{F}\left(F - 1 + \frac{\sqrt{Tu} + \sqrt{Tb}}{\sqrt{Tu}}\cos\alpha\right)A. \tag{36}$$

5. Conclusions. The compactness degree index characterizes in the most complex manner the woven structure, through the fact that gathers, within a well-defined mathematical relation, all basic parameters of a woven fabric, such as: fineness of

yarns, expressed by the d_u and d_b diameter of yarns; thickness by Pu and Pb, the link by the Ru and Rb weave repeat, and number of passing t_u and t_b.

Also, the compactness degree offers to both designers and technologists some concrete elements on the utilization of the capacity of woven filling with yarns and, starting from this, a behavioural model in the process of woven fabrication.

The maximum limit of the compactness degree is 100% and it can be exceeded only when employing low density fibers, obtained by card spinning and with low torsion.

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ALGORITM PENTRU CALCULUL GRADULUI DE COMPACTITATE AL ŢESĂTURILOR

I. Gradul de compactitate pentru ţesături simple

(Rezumat)

Se prezintă un algoritm de calcul al gradului de compactitate prin care se stabilesc relaţii matematice precise între parametrii de bază ai structurii ţesute: densitatea de lungime şi desimea sistemelor de fire, legătura şi materia primă. Gradul de compactitate astfel descris reprezintă cel mai complex indice de caracterizare a ţesăturilor, constituind în acelaşi timp bază de proiectare raţională a ţesăturilor.

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Secţia VIII
TEXTILE. PIELĂRIE

AN ALGORYTHM FOR THE CALCULATION OF WOVENS COMPACTNESS DEGREE

II. COMPACTNESS DEGREE FOR SEMIDOUBLE WARP WOVENS

BY
GABRIEL CORNELIU CHINCIU, DANIEL CHINCIU and IRINA CRISTIAN

1. Introduction. Semidouble warp wovens are made of three systems of yarns, two of which as a warp and one a weft system. The ratio of the warp systems may be $1Us : 1Ui$, $2Us : 1Ui$, $3Us : 1Ui$, as a function of the product final destination.

The compactness degree is an important characteristic of wovens with compound interlacing weaves, representing an useful designing mark in establishing the wovens' basic parameters, on considering the possible obtainment of suitable functional characteristics.

For compound woven materials, the compactness degree is calculated separately on systems of yarns followed by summ as depending on the type of interlacing weave, for the obtainment of the woven's compactness degree.

The compactness degree on the warp system is calculated [1],[2] as follows:

$$K_{u_x} = \frac{P_{u_x}}{P_{u_x \max}} \cdot 100, \quad (1) \qquad Kb = \frac{Pb}{Pb_{\max}} \cdot 100, \quad (2)$$

while, for the woven fabric, the compactness degree is calculated with the relation:

$$Kt = \frac{\sum_{x=1}^{m} Ku_x + Kb}{m+1}, \quad (3)$$

where m is number of warp systems.

Knowing that:

$$Pu_x \max = \frac{Ru_x}{L_{Ru_x}} \cdot 100 \quad (4)$$

and

$$K_{ux} = \frac{P_{ux}}{P_{ux \max}} \cdot 100 \quad (5)$$

and substituting (4) and (5) in relations (1) and (2), one may obtain:

$$Ku_x = \frac{Pu_x \cdot L_{Ru_x}}{Ru_x}, \quad (6) \qquad Kb = \frac{Pb \cdot L_{Rb}}{Rb}, \quad (7)$$

where: Ru_x is warp repeat (x); Rb – weft repeat; L_{Rux} – length of the warp repeat (x); L_{Rb} – length of the weft repeat.

2. Calculation of the Compactness Degree of the Warp Systems. Maximum thickness values, Pu_x max, are calculated from the cross sections plotted in Fig.1, where the superior warp is noted with (s), and the inferior one with (i).

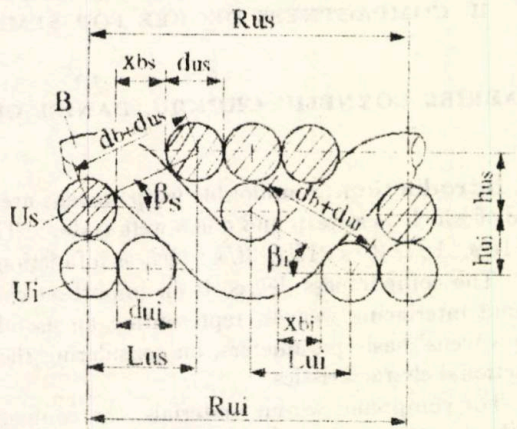

Fig. 1.– Semidouble warp woven fabric. Cross section. Maximum technological thickness.

For the higher warp, there results that:

$$L_{Ru_s} = Ru_s \cdot d_{us} + x_{bs} \cdot t_{bs}, \quad (8) \qquad x_{bs} = Lu_s - d_{us}, \quad (9)$$

where:

$$Lu_s = (d_{us} + d_b) \cdot \cos\beta_s = Ds \cdot \cos\beta_s, \quad (10)$$

$$x_{bs} = (d_{us} + d_b) \cdot \cos\beta_s - d_{us} = Ds \cdot \cos\beta_s - d_{us}, \quad (11)$$

so that:

$$L_{Ru_s} = Ru_s \cdot d_{us} + (Ds \cdot \cos\beta_s - d_{us}) \cdot t_{bs}, \quad (12)$$

while:

$$Ku_s = \frac{Pu_s[Ru_s \cdot d_{us} + (Ds \cdot \cos\beta_s - d_{us}) \cdot t_{bs}]}{Ru_s}, \quad (13)$$

in which: L_{Rus} is length of the high warp repeat; Ru_s – warp repeat corresponding to the high warp; d_{us} – diameter of the high warp yarns; d_b – diameter of the weft yarns; β_s – waving angle of the high warp, as a result of the interlace with the

unique weft yarns; t_{bs} – number of passings of the unique weft through the yarns of the high weft as part of a warp ratio.

For the low warp, the compactness degree is calculated with relation (6), in which:

$$L_{Ru_i} = Ru_i \cdot d_{ui} + (D_i \cdot \cos\beta_i - d_{ui})t_{bi}, \tag{14}$$

$$Ku_i = \frac{Pu_i \cdot [Ru_i \cdot d_{ui} + (D_i \cdot \cos\beta_i - d_{ui}) \cdot t_{bi}]}{Ru_i}, \tag{15}$$

where: L_{Rui} is length of the low warp repeat; R_{ui} – warp repeat corresponding to the low warp; d_{ui} – diameter of the low warp yarns; β_i – waving angle of the low warp, as a result of the interlace with the unique weft yarns; t_{bi} – number of passings of the unique weft through the yarns of the low weft as part of a warp ratio.

3. Calculation of the Compactness Degree of the Warp System.

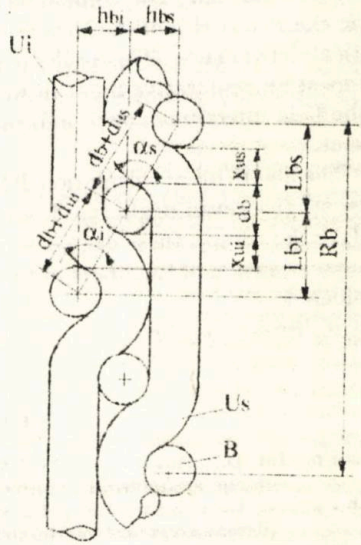

Fig. 2.– Semidouble warp wovens. Longitudinal section. Maximum technological thickness.

The compactness degree is calculated from relation (7), where L_{Rb} is calculated according to the scheme plotted in Fig.2, the following algorithm being applied:

$$L_{Rb} = Rb \cdot d_b + x_{us} \cdot t_{us} + x_{ui} \cdot t_{ui}, \tag{16}$$

where:

$$x_{us} = L_{bs} - d_b, \quad (17) \qquad x_{ui} = L_{bi} - d_b, \tag{18}$$

while:

$$Lb_s = (d_{us} + d_b) \cdot \cos \alpha_s = D_s \cdot \cos \alpha_s, \tag{19}$$

$$Lb_i = (d_{ui} + d_b) \cdot \cos \alpha_i = D_i \cdot \cos \alpha_i \tag{20}$$

After substituting the values from (19) and (20) into (16), there results:

$$L_{Rb} = Rb \cdot d_b + (Ds \cdot \cos \alpha_s - d_b) \cdot t_{us} + (Di \cdot \cos \alpha_i - d_b) \cdot t_{ui}, \tag{21}$$

while substitution of the value from (21) into (6) gives relation (22), to be applied in the calculation of the compactness degree of the weft system:

$$K_b = \frac{Pb \cdot [Rb \cdot d_b + (Ds \cdot \cos \alpha_s - d_b) \cdot t_{us} + (Di \cdot \cos \alpha_i - d_b) \cdot t_{ui}]}{Rb}, \tag{22}$$

where: a_s is waving angle of the weft, as due to its interlacing with the yarns of the high warp; a_i – waving angle of the weft, as due to its interlacing with the yarns of the low warp; t_{us}, t_{ui} – number of passings of the high and, respectively, of the low warp, through the yarns of the unique weft as part of ratio.

4. Conclusions. The compactness degree index describes most completely the basic characteristics of the wovens' structure, expressed as a most rigurous mathematical dependence. This is the reason why – especially in the case of wool – it is the most representative mark in wovens designing, the more so that the literature of the field offers but scarce information on the compactness degree of compound wovens.

The algotitms of calculation discussed in the paper bring light – on one side – in a less studied, even neglected domain of scientific interest while, on the other side, analyze the compactness degree of compound structures against the background of the real situation of the fibers in the woven fabric, specific for the type of structure considered.

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ALGORITM PENTRU CALCULUL GRADULUI DE COMPACTITATE AL ŢESĂTURILOR
II. Gradul de compactitate pentru ţesături semiduble de urzeală

(Rezumat)

Se descrie un algoritm pentru calculul gradului de umplere pentru structuri ţesute semiduble de urzeală. Prin conţinut şi mod de rezolvare lucrarea reprezintă o noutate în domeniu, deoarece literatura de specialitate nu prezintă un model de rezolvare a acestei probleme.

Modul de prezentare şi succesiunea calculelor constituie o bază pentru elaborarea unui program de proiectare asistată de calculator.

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AN ALGORYTHM FOR THE CALCULATION OF WOVENS COMPACTNESS DEGREE
III. THE COMPACTNESS DEGREE FOR SEMIDOUBLE WEFT WOVEN MATERIALS

BY
IRINA CRISTIAN, DANIEL CHINCIU and GABRIEL CORNELIU CHINCIU

1. Introduction. Semidouble weft wovens are formed of three fiber systems – i.e., a warp and, respectively, two weft systems. From a technological point of view, semidouble weft wovens are different from semidouble warp ones, involving mainly technology of weft preparation much more simple than that of warp preparation, which is advantageous for weft semidoubles; nevertheless, the weaving field is half that of the warp semidoubles. The two elements are essential in making the production decision.

The compactness degree on systems is calculated by the following relations [1], [2]:

$$Ku = \frac{Pu}{Pu\,\max} \cdot 100, \tag{1}$$

$$Kb_y = \frac{Pb_y}{Pb_y\,\max} \cdot 100, \tag{2}$$

while for the woven material:

$$Kt = \frac{Ku + \sum_{y=1}^{n} Kb_y}{1+n} \tag{3}$$

where n is the number of weft systems.

2. Calculation of the Compactness Degree of the Warp System. Length of the ratio in warp for a woven material with maximum technological thickness is calculated as presented in Fig.1.

$$L_{Ru} = Ru \cdot d_u + x_{bs} \cdot t_{bs} + x_{bi} \cdot t_{bi}, \tag{4}$$

$$x_{bs} = Lu_s - d_u, \tag{5}$$

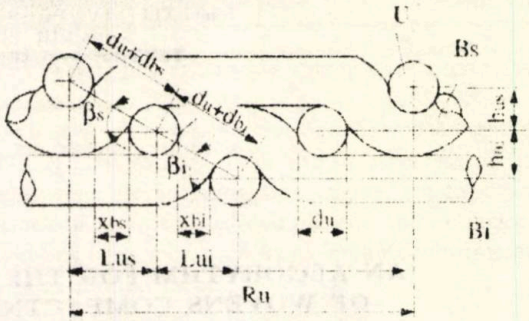

Fig. 1.– Semidouble weft woven fabric. Cross section. Maximum technological thickness.

$$x_{bi} = Lu_i - d_u, \tag{6}$$

$$Lu_s = (d_u + d_{bs}) \cdot \cos\beta_s = Ds \cdot \cos\beta_s, \tag{7}$$

$$Lu_i = (d_u + d_{bi}) \cdot \cos\beta_i = Di \cdot \cos\beta_i, \tag{8}$$

$$L_{Ru} = Ru \cdot d_u + (Ds \cdot \cos\beta_s - d_u) \cdot t_{bs} + (Di \cdot \cos\beta_i - d_u) \cdot t_{bi}, \tag{9}$$

$$Ku = \frac{Pu \cdot [Ru \cdot d_u + (Ds \cdot \cos\beta_s - d_u) \cdot t_{bs} + (Di \cdot \cos\beta_i - d_u) \cdot t_{bi}]}{Ru}, \tag{10}$$

where: β_s is waving angle of the warp as due to its interlacing with the high weft; β_i – waving angle of the warp as due to its interlacing with the low weft; t_{bs}, t_{bi} – number of passings of the high and, respectively, low weft, through the unique fibers of warp within a ratio.

3. Calculation of the Compactness Degree of the Weft System. The compactness degree is calculated with relation (2), where:

$$Pb_{y\,max} = \frac{Rb_y}{L_{Rby}} \cdot 100, \tag{11}$$

where length of the weft ratio, L_{Rby}, is calculated with the scheme plotted in Fig.2, for the two – low (i) and high (s) – weft systems.

For the calculation of the compactness degree of the high weft, length of the system ratio, L_{Rbs}, is calculated with the relation:

$$L_{Rbs} = Rb_s \cdot d_{bs} + x_{us} \cdot t_{us}, \tag{12}$$

where:

$$x_{us} = Lb_s - d_{bs}, \tag{13}$$

while:

$$Lb_s = (d_u + d_{bs}) \cdot \cos\alpha_s = Ds \cdot \cos\alpha_s. \tag{14}$$

Substituting (14) into (11) and then in (2), there results:

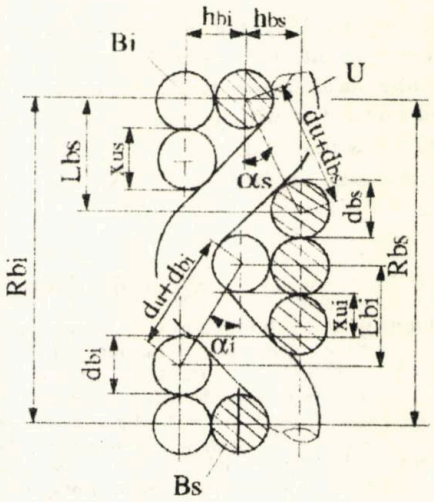

Fig. 2.– Semidouble weft woven fabric. Longitudinal section. Maximum technological thickness.

$$Kb_s = \frac{Pb_s \cdot [Rb_s \cdot d_{bs} + (Ds \cdot \cos\alpha_s - d_{bs})t_{us}]}{Rb_s}, \tag{15}$$

where: α_s is waving angle of the high weft as a result of its interlacing with unique warp; t_{us} – number of passings of the unique warp through the high weft fibers within a ratio.

The compactness degree for the low weft is calculated with the following relations:

$$L_{Rbi} = Rb_i \cdot d_{bi} + x_{ui} \cdot t_{ui}, \tag{16}$$

where:

$$x_{ui} = Lb_i - d_{bi}, \tag{17}$$

$$Lb_i = (d_u + d_{bi}) \cdot \cos a_i = Di \cdot \cos\alpha_i, \tag{18}$$

resulting:

$$Kbi = \frac{Pb_i \cdot [Rb_i \cdot d_{bi} + (Di \cdot \cos\alpha_i - d_{bi}) \cdot t_{ui}]}{Rb_i} \tag{19}$$

in which: α_i is the waving angle of the low weft, as due to the interlacing with unique warp; t_{ui} – number of passing of the unique warp through the low weft's fibers, as part of a ratio.

4. Conclusions. The compactness degree, viewed both as to its content and calculation algorithm, creates precise mathematical relations between the woven's basic parameters, thus characterizing any woven structure in the most complex possible way.

In modern designing of wovens [3], [4], aimed at optimizing their structural parameters so that their contribution in utilization processes should be maximum, the compactness degree is a key factor in the establishment of a new computer – aided method of wovens designing, with special application to those employing wool as a raw material.

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ALGORITM PENTRU CALCULUL GRADULUI DE COMPACTITATE AL ŢESĂTURILOR
III. Gradul de compactitate pentru ţesături semiduble de bătătură

(Rezumat)

Se descrie un algoritm pentru calculul gradului de umplere pentru structuri ţesute semiduble de bătătură. Pornind de la considerentul că gradul de umplere este un raport procentual între desimea reală şi desimea maximă a sistemelor de fire, el se constituie într-un important reper de proiectare, mai ales în domeniul structurilor ţesute formate din mai multe sisteme de fire (> 2). Se recomandă ca gradul de umplere să fie folosit în elaborarea programelor de proiectare asistată de calculator pentru structuri ţesute din fire tip lână, dar şi din celelalte materii prime.

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Secţia VIII
TEXTILE. PIELĂRIE

THE IMPORTANCE OF ZETA POTENTIAL IN THE CHEMICAL TEXTILE FINISHING

I. POSSIBILITIES TO INCREASE THE FIXATION EFFICIENCY IN FIBRE-REACTIVE DYES SYSTEMS*)

BY

E. POPPEL, R. MUREŞAN, A. MUREŞAN and C. MĂLUŢAN

1. Introduction. Measuring of electrokinetic potential hasn't imposed yet like a method for the control and the dirigibility of the process from the textile industry, because the technique of measuring and the theoretical base is a little known or often is vague due to the factors of multiple influence on zeta potential of textile materials.

In the present paper had been tried the use of zeta potential in the textile research orientated into practice, starting from the possibilities of measuring from which we dispose and the results obtained contribute to the understanding of different modifications what take place in the textile materials structure during the finishing operations.

Such modifications take place and during the dyeing process or/and crosslinking finish of cotton materials [1],...,[6].

Starting from the known advantages in dyeing with reactive dyes (various palette of colours, brighting nuances, good strengths), but also from the disadvantages due to the low degree of fixing of these dyes (dyeing efficiency 40-70%) has tried a fixing process of reactive dye simultaneously with a treatment of crosslinking finish for improving dyeability with reactive dyes.

2. Experimental. The dyeings were carried on a cotton material after a continuous process, the variant: pad – dry – cure. The padding operation was realizing with a solution that contains: 10 g/l Reactive Red 58; x g/l $MgCl_2$; y g/l Depremol G (reticulation agent). The padded samples were dried and cured at 150°C for 3 min. Finally were carried a soaping in alkaline medium (10 g/l Na_2CO_3 and 2 g/l nonionic detergent at 60-70°C, 20 min) followed by rinses with hot and cold water.

For apreciating the efficiency of the mentioned treatment were calculated: K/S (a characteristic parameter of the dyeing process, generally based on the Kubelka-

*) The present note takes part from a vaster research programme which is elaborating now at Technical University, Jassy.

Munk relation ship between spectral reflectance R, the Kubelka-Munk spectral absorption constant K and the spectral scattering constant S) [7] like a measure of colour yield from the dyed samples, the quality index of fabric by the determination of textile material strength and renewing angle, and also the electrokinetic potential like a control measure of modifications which appear as a result of the dyeing and the crosslinking finish [8].

3. Results and Discussion. The obtained results are materialized in the Figs. 1, 2 and the Tables 1, 2.

From the comparison of the colour yield difference (appreciated with the K/S value) between the dyed samples and those dyed and soaped, we notice that these decrease with the improving of Depremol G concentration in solution (Fig.1).

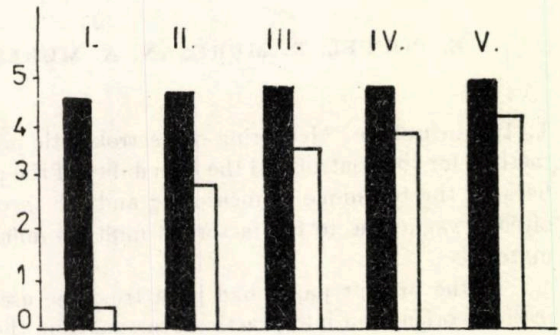

Fig. 1.– Comparison of colour yield for dyeing of Reactive Red 58 on variable concentrations of Depremol G and invariable of $MgCl_2$ (16 g/l). I – 0 g/l Depremol G; II – 30 g/l Depremol G; III – 75 g/l Depremol G; IV – 120 g/l Depremol G; V – 150 g/l Depremol G.

The same thing illustrates the Fig.2, too. With the improving of $MgCl_2$ concentration from the padding liquor, the colour yield difference between the dyed samples and those dyed and soaped decreases (Fig.2).

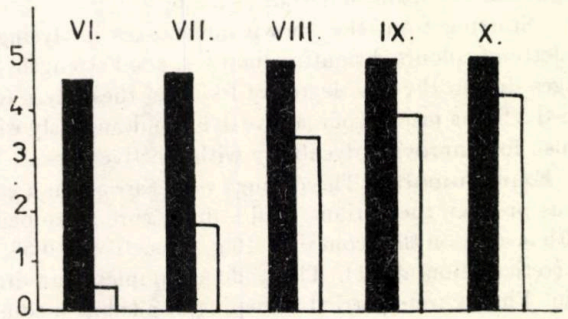

Fig. 2.– Comparison of colour yield obtained for dyeing of Reactive Red 58 on variable concentrations of $MgCl_2$ and invariable concentration of Depremol G (150 g/l). VI – 0 g/l $MgCl_2$; VII – 8 g/l $MgCl_2$; VIII – 15 g/l $MgCl_2$; IX – 24 g/l $MgCl_2$; X – 30 g/l $MgCl_2$.

Between the dyed samples and unsoaped don't notice the essential differences of the colour yield no matter what quantity of auxiliaries from padding solution.

The textile strength decreases as the result of the reticulation treatment, the decreasing varying proportionally with the increasing of reticulation agent con-

Table 1

Sample	Textile strength N	Renewing angle	The quality index
M	368	57	-
I	342	59	0.693
II	315	65	0.704
III	284	90	0.879
IV	256	125	1.1
V	220	150	1.134
VI	350	60	0.553
VII	300	95	0.980
VIII	240	126	1.039
IX	226	134	1.041
X	178	148	0.905

centration, respectively the $MgCl_2$ quantity, a more obviously decreasing beeing ascertain in the case of the $MgCl_2$ concentration increasing (Table 1).

The presence of reticulation agent takes to the increasing of the renewing angle of the textile material; the angle value depends both on the reticulation agent concentration and the $MgCl_2$ concentration from padded solution.

Correlating the main index: the textile strength and the renewing angle we have calculated the total quality index I_c [8], which values are presented in the Table 1.

From this point of vue are recommended the reticulation agent concentrations of 120-150 g/l and for $MgCl_2$ of 8-24 g/l.

The modifications of superficial density charge, respectively the zeta potential of cotton textile material are illustrated in the Table 2. The zeta potential was determined by the streaming potential method [8].

Table 2

Sample	Electrokinetic potential, [mV]
M	-49
I	-33
II	-35.69
III	-40.18
IV	-41.68
V	-42.76
VI	-100.82
VII	-60.39
VIII	-45.86
IX	-42.38
X	-38.31

The presence only of $MgCl_2$ like electrolite in the padding solution (sample I) – so as it to expect – decreases the negative zeta potential value; this value decreases with the increasing of the $MgCl_2$ concentration (the samples VII-X).

By adding the reticulation agent (in the presence of $MgCl_2$ like an acid catalizer), it reacts with the cotton OH groups, and the modifications which appear being illustrated too, by an increasing of the negative zeta potential (the samples II-V).

The carbonyl groups of Depremol G influence by their polarity the zeta potential of the cellulosic fibre. In this way, it is ascertained that in the absence of $MgCl_2$, when the reticulation reaction doesn't take part, the negative value of zeta potential is maximum (sample VI), and the quality index is minimum.

4. Conclusions. The obtained results conclude the following:

1. By simultaneous application of a dyeing process with a crosslinking finish process results:

– the increasing of fixation efficiency of reactive dyes;

– the reduction of the operation number from technologic flux of finishing.

2. By measurings of zeta potential, the modifications which appear on the cellulosic material structure in the presence of the different auxiliaries from the padding liquor can be appreciated and even controled.

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ROLUL POTENŢIALULUI ZETA ÎN FINISAREA CHIMICĂ TEXTILĂ

(Rezumat)

Concomitent cu tratamentele de neşifonabilizare se efectuează şi o vopsire cu coloranţi reactivi. Ca agent de neşifonabilizare se utilizează Depremol G şi drept catalizator $MgCl_2$. Cantitatea de colorant fixată depinde de concentraţia agentului de reticulare precum şi de cea a catalizatorului. Modificările care apar în structura celulozei sunt analizate şi din punct de vedere al potenţialului zeta.

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Secţia VIII
TEXTILE. PIELĂRIE

A MATHEMATICAL MODEL OF TEXTILE WASTE WATER DECOLORISATION WITH SODIUM DITHIONITE

BY

ANDREI BERTEA, ROMEN BUTNARU,
ANIŞOARA BERTEA and NICULINA VRÎNCEANU

1. Introduction. One of the major ecological problems that textile industry is forced to face is the problem of colored waste waters. The presence of dyestuffs in these waters is often more an aesthetical problem than an ecological one, but nevertheless it must be solved. Until now there is not any general technique capable to solve all the colored waste waters problems. Any specific situation must be carefully analyzed, considering the local conditions: dyestuffs and chemicals that have been used, their concentration, the average waste water flow, the effluent maximum and minimum flow, the local drainage characteristics and the specific of the waste water treatment plant. The whole of these factors determines the choice of the technique that provides best results [1], [2].

As biological treatment is not efficient for waste water treatment, because the biodegradability of most dyestuffs is very scarce, the decolorisation treatments are of physical or chemical nature [3],...,[6]. One of the most used chemical treatments use reducing or oxidizing substances. The reducer that is usual to the textile industry that can be used to remove color from waste waters is the sodium dithionite. This reducing agent, as the oxidizing agents as well, is destroying the chromophore of the azoic dyestuff, transforming the azoic group into two amino groups:

$$R_1 - C_6H_4 - N = N - C_6H_4 - R_2 + 2S_2O_4^{2-} \Rightarrow R_1 - C_6H_4 - NH_2 + \\ + R_2 - C_6H_4 - NH_2 + 4SO_3^{2-}$$

In a previous paper [7] there has been studied the way that four acid dyestuffs and four reactive dyestuffs can be transformed into uncolored substances using sodium dithionite. The selection of those classes of dyestuffs has been made considering their low capability of adsorbtion on the activated sludge in a biological plant. The study came to the conclusion that such treatment is efficient, and that its application might be profitable, if the problem of the sulfate ion increase can be solved. The present study is trying to find a mathematical model for the sodium

dithionite decolorisation process, to better understand the role of each parameter and to find the ways of optimizing it.

2. Experiments. Two dyestuffs, an acid one and a reactive one, have been tested: Acid Red 6A and Reactive Black MN. The evaluation of the effectiveness of the decolorisation treatment was made using the decolorisation degree, which is the ratio between the decrease of extinction for a treated sample and the extinction of an untreated one. The extinction has been measured using a photocolorimeter, using the filter that gives maximum extinction values.

$$\text{Decolorisation degree} = \frac{E_{untreated} - E_{treated}}{E_{untreated}} \cdot 100$$

To find out the mathematical model a three independent variables rotable central composed program has been used [8]. The three independent variables that have been chosen were: x_1 – dyestuff concentration, in mg/l; x_2 – dyestuff concentration, in g/l; x_3 – pH value. The codification of the parameters is shown in Table 1.

Table 1

The Codification of the Parameters

Code	-1.682	-1	0	1	1.682
Dyestuff concentration, mg/l	2	5	10	15	18
Dithionite concentration, g/l	0.5	1.1	2	2.9	3.5
pH	2	4	7	10	12

The results have been processed using a Texpro program and a PGA computer. For the acid dyestuff there have been found the following relations.

The regression equation is:

$$Y = 109.944 - 2.14x_1 + 1.905x_2 - 8.92x_3 - 29.07x_1^2 - 5.97x_2^2 - \\ - 21.248x_3^2 - 0.179x_1x_2 - 2.604x_1x_3 + 0.6x_2x_3$$

Testing the parameters of the regression equation using a Student test we have found that the tabled value for the test is 2.132, with $\alpha = 0.95$ and $\nu = 4$, and the values of the test for each coefficient are:

$Tb_0 = 348.445$ – b_0 significant
$Tb_1 = -10.224$ – b_1 significant
$Tb_2 = 9.099$ – b_2 significant
$Tb_3 = -42.612$ – b_3 significant
$Tb_{11} = -142.515$ – b_{11} significant
$Tb_{22} = -29.269$ – b_{22} significant
$Tb_{33} = -104.165$ – b_{33} significant
$Tb_{12} = -0.653$ – b_{12} insignificant
$Tb_{13} = -9.517$ – b_{13} significant

The coordinates of the critical point are: $x_1 = -0.028$; $x_2 = 0.342$; $x_3 = -0.203$, which is a maximum point.

The graphs that show the variation of the purpose function in relation with two of the three independent variables are presented in Figs.1,...,6.

For the reactive dyestuff there have been found the following regression equation:

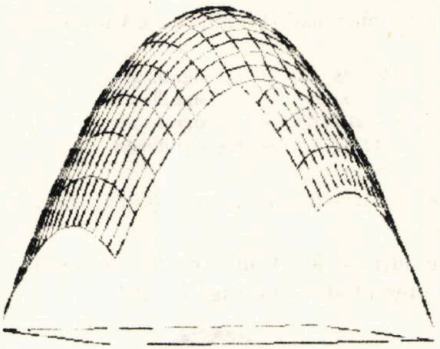

Fig. 1.- $Y = f(x_1, x_2, 0)$

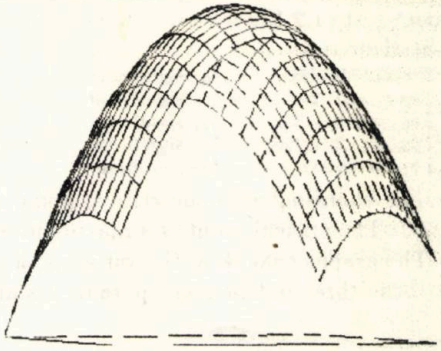

Fig. 2.- $Y = f(x_1, 0, x_3)$

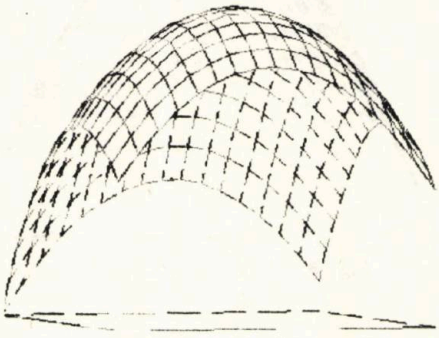

Fig. 3.- $Y = f(0, x_2, x_3)$

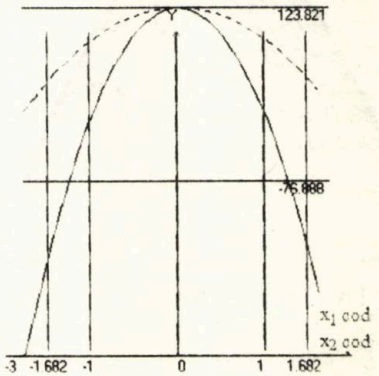

Fig. 4.- $Y(x_1, 0, 0)\cdots$; $Y(0, x_2, 0)$——

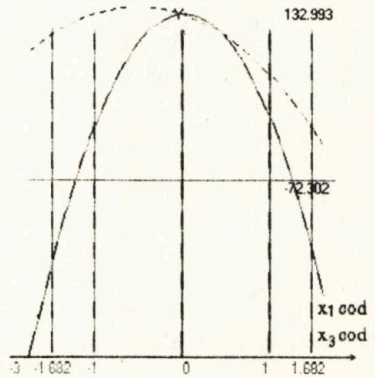

Fig. 5.- $Y(x_1, 0, 0)\cdots$; $Y(0, 0, x_3)$——

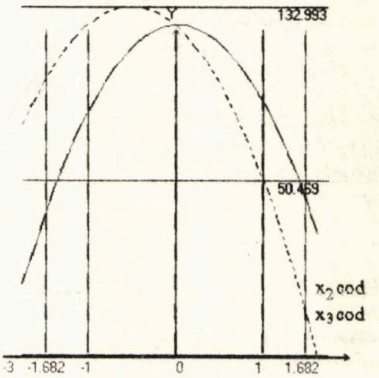

Fig. 6.- $Y(0, x_2, 0)\cdots$; $Y(0, 0, x_3)$——

$$Y = 123.821 + 3.478x_1 + 1.364x_2 - 21.289x_3 - 43.443x_1^2 - 13.039x_2^2 - \\ - 12.279x_3^2 + 9.687x_1x_2 + 4.337x_1x_3 + 1.15x_2x_3$$

Testing the parameters of the regression equation for a tabled value for the

Student test of 2.132 with $\alpha = 0.95$ and $\nu = 4$ we obtained the following values for the Student test:

$Tb_0 = 1310.674$	–	b_0 significant	$Tb_1 = 55.488$	–	b_1 significant
$Tb_2 = 21.762$	–	b_2 significant	$Tb_3 = -339.665$	–	b_3 significant
$Tb_{11} = -711.332$	–	b_{11} significant	$Tb_{22} = -213.506$	–	b_{22} significant
$Tb_{33} = -201.056$	–	b_{33} significant	$Tb_{12} = 118.272$	–	b_{12} significant
$Tb_{13} = 52.952$	–	b_{13} significant			

The coordinates of the critical point are: $x_1 = -0.007$; $x_2 = -0.034$; $x_3 = -0.870$. The critical point is a maximum one.

The graphs that show the variation of the purpose function in correlation with two of the three independent parameters are presented in the Figs.7,...,12.

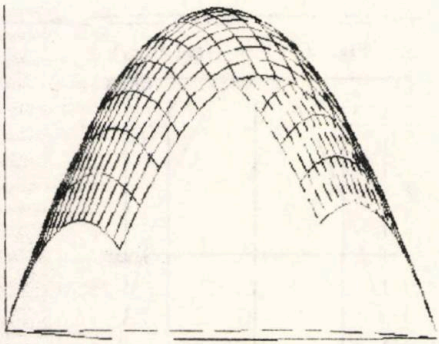

Fig. 7.– $Y = f(x_1, x_2, 0)$

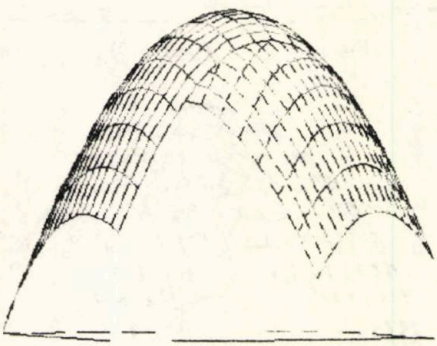

Fig. 8.– $Y = f(x_1, 0, x_3)$

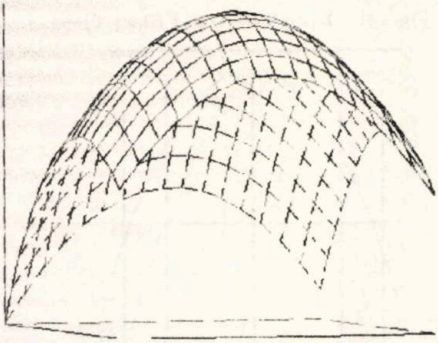

Fig. 9.– $Y = f(0, x_2, x_3)$

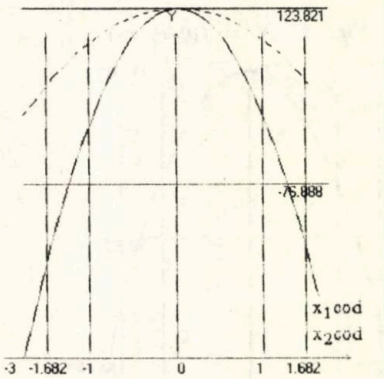

Fig. 10.– $Y(x_1, 0, 0) \cdots$; $Y(0, x_2, 0)$——

3. Discussion of the Results. Analyzing the regression function obtained for the decolorisation of the acid dyestuff one can see that increasing the sodium dithionite concentration the effectiveness of the decolorisation is bigger. In opposition, the increase of the dyestuff concentration leads to scarce decolorisation degrees. The influence of the first factor is of main importance, as it can be seen from the positive

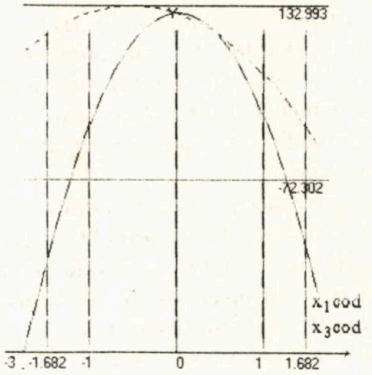

Fig. 11.- $Y(x_1,0,0)\cdots$; $Y(0,0,x_3)$——

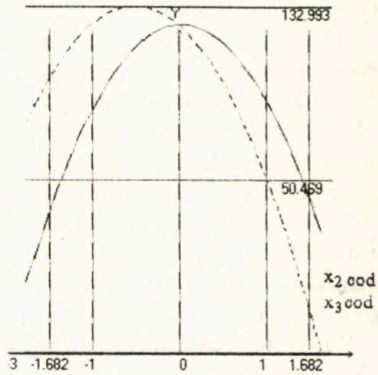

Fig. 12.- $Y(0,x_2,0)\cdots$; $Y(0,0,x_3)$——

coefficient of the term x_1x_2. The increase of the pH value is completely detrimental to the decolorisation process, because the coefficient of the term x_3 and x_1x_3 have big negative values. This latest fact may lead to the conclusion that the increase of the pH value, even at high sodium dithionite concentration, provides very low decolorisation degrees.

From graphs 1 and 2 it can be seen that at constant pH value (equal to 7), the maximum decolorisation degree values are obtained when the sodium dithionite concentration is lesser than 1.5 g/l. If the sodium dithionite concentration surpasses this value, the decolorisation degree decreases. This effect is stronger as the dyestuff concentration in the waste water is bigger. The optimum ratio between the dyestuff concentration and the sodium dithionite concentration is of 100 g per 1 g acid dyestuff.

The graphs 3 and 4 show that at a constant sodium dithionite concentration of 2 g/l the maximum values for the decoloration degree are obtained at a neutral pH value, when the dyestuff concentration is not bigger than 8 mg/l. When the dyestuff concentration increases, especially at alkaline pH values, the decolorisation degree is very low.

From graphs 5 and 6 it can be observed that at a constant dyestuff concentration of 10 mg/l the optimum dithionite concentration is 100-150 g per 1 g of acid dyestuff, and the best decolorisation degrees are obtained when the pH is neutral. An increase of the sodium dithionite concentration, especially when the pH is strongly acid (< 3), is followed by the severe decrease of the decolorisation degree.

The maximum value of the decolorisation degree for Acid Red 6A is obtained in the following conditions: concentration of dyestuff equal to 9.86 mg/l, sodium dithionite concentration equal to 2.307 g/l and the pH value equal to 7.6.

Analyzing the purpose function for the decolorisation of the reactive dyestuff, it can be observed that terms x_1^2 and x_3 have negative coefficient, which means that the increase of these parameters produces a decrease of the decolorisation degree. The fact that the terms x_1x_2, x_1x_3 and x_2x_3 have positive coefficients may lead to the conclusion that the detrimental effects of dyestuff concentration and pH value

increase can be counteracted by the increase of the dithionite concentration.

The graphs 7 and 8 show that at a neutral pH value the maximum values for the decolorisation degree are obtained when the dyestuff concentration is in the range of 10-15 mg/l, and the concentration of reducing agent is 2 g/l. Any increase in the dyestuff concentration or decrease of the sodium dithionite concentration is followed by the decrease of the decolorisation degree.

From graphs 9 and 10 it can be seen that at a concentration of sodium dithionite of 2 g/l, the maximum values of the decolorisation degree are obtained when the dyestuff concentration is not bigger than 10 mg/l, and the pH value is in the neutral zone. When the concentration of the dyestuff increases the decolorisation degree decreases strongly, especially when the pH values are lesser than 7.

When the dyestuff concentration is 10 g/l, as it can be seen from Figs. 11 and 12, best results are obtained at relative low reducing agent concentration (about 1 g/l), when the pH is neutral.

The maximum decolorisation degree for the reactive dyestuff is obtained at a dyestuff concentration of 9.96 g/l, a sodium dithionite concentration of 1.97 g/l and a pH value of 4.5.

4. Conclusions. The optimum dyestuff/sodium dithionite ratio varies from dyestuff to dyestuff. For Acid Red A this ratio is 100 g per 1 g dyestuff, and for Reactive Black MN the ratio is 150 g per 1 g dyestuff. In these conditions the decolorisation degree is almost 100%. The process does not produce any sediments, and that is one of its great advantages. The effect of the temperature is relatively low, and the best results are obtained at a pH value close to the neutral range in the case or the acid dye and at an acid pH for the reactive one.

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UN MODEL MATEMATIC AL DECOLORĂRII APELOR UZATE TEXTILE CU DITIONIT DE SODIU

(Rezumat)

Se propune un model matematic al procesului de decolorare a apelor uzate textile ce conţin coloranţi acizi sau reactivi, obţinut prin utilizarea unui program rotabil compus, şi se stabilesc condiţiile optime de tratare.

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CONTRIBUTION À LA CONNAISSANCE DU PHÉNOMÈNE D'APLATISSEMENT DES FILS AU TISSAGE

PAR
MARIN DINU et VALERIA NISTOR

1. Introduction. Dans la pratique industrielle on a observé que dans les tissus en fibres synthétique 100% ou leurs mélanges avec de la laine, quand la température monte comme résultat du frottement et de l'action des forces de compression, il apparaît le défaut d'écrasement des fibres qui modifie leur aspect fondamental, la fibre ayant finalement une section transversale du type semiluné. Dans le cas des frottements non-accompagnés par l'effet d'écrasement, la partie soumise au frottement apparaît comme une fibre fondue qui change sa couleur vers blanc mat, avec extension d'environ 15-20% vers l'extérieur de la partie affectée. Il faut retenir le fait que tant les fibres synthétiques obtenues par le procédé de polymérisation que celles obtenues par le procédé de polycondensation présentent les mêmes caractéristiques quand elles sont soumises aux sollicitations énumerées antérieurement.

Plus le pourcentage en fibres synthétiques s'accroît dans le mélange du lot, plus le lot respectif présentera le danger de l'apparition de l'aplatissement dans les opérations de tissage.

Le tendance de nuançage des fibres aplaties est vers la couleur claire, parfois conduisant à un défaut de fils en groupe.

2. Partie expérimentale. En analysant les régions où peuvent apparaître les aplatissements on a constaté qu'ils apparaissent dans les opérations suivantes du processus de tissage: bobinage, cannetage et tissage.

Au bobinage on a remarqué que l'apparition de phénomène coincide avec le déréglage du système d'élevement de la bobine du tambour qui conduit au frottement de celle-ci sur le tambour et à l'apparition des fils aplatis plus intensément pour les couleurs foncées.

Les fils aplatis peuvent également apparaître durant l'opération de cannetage à cause du blocage du galet palpateur et du blocage de l'avancement du fuseau (à cause de la cannelure de la came spatiale et de la fatigue des ressorts ce qui mène à des frottements répétés).

On a observé que dans le cas des métieres à tisser les fils aplatis peuvent apparaître tant dans le chaine que dans le trame. Dans la direction de la chaîne les fils aplatis peuvent apparaître dans les régions suivantes: là où se forme la foule; à l'ouverture du tissu. Ces fibres sont trés peu visibles dans le tissu écru, mais elles

deviennent évidentes après lénnoblissement textile.

Dans la zone de formation de la foule les fils s'aplatissent à cause du réglage incorrect de la hauteur de la foule par rapport au bord supérieur de la navette et par le réglage en avance par rapport au diagrame cyclique du moment de l'ouverture de la foule. Dans la direction de la trame, les régions où peuvent apparaître des fils aplatis sont: à environ 65 cm du bord de la boîte vers la milieu du tissu; dans la région du temple; dans la région de la fourchette; dispersés sur toute la largeur du tissu. L'apparition de ce phénomène dans la direction de la trame est due au réglage incorrect du mécanisme de lancement de la navette, des boîtes, de la fourchette et des temples.

D'autres causes qui mènent à l'apparition des fils aplatis dans la direction de la trame sont les déréglages à la navette comme: la destruction du canal de protection du fil qui se trouve sur la partie latérale de la navette et l'usure du tablier de freinage du fil dans la navette.

Le plus souvent on trouve des fils aplatis dans direction de la trame.

3. Resultats et discussions. Sur les tissus qui contiennent de la fibre en polyester teints en couleurs foncées on observe parfois des fibres qui paraissent optiquement plus claires que le fond du tissu tant dans la chaîne que dans la trame.

Ces fils paraissent répartis non-uniformément comme position et longueur (Figs. 1 et 2) et sont connus en pratique sous le nom de *fils aplatis.*

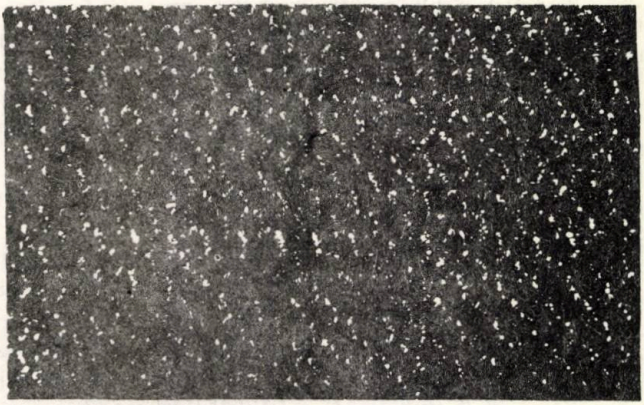

Fig. 1.– Bande blanchâtre (fils aplatis inégalement répartis sur une longueur de 1-2 cm).

L'image microscopique des fibres qui entrent dans la composition du fil indique des fibres en polyester qui ont subi l'influence des actions mécano-thermiques d'écrasement, dégradation et déformation des fibres sur certaines régions comme suite du métier à tisser (Figs. 3,...,9).

Parce que les régions dégradées se présentent seulement à la surface et pas à l'intérieur du fil fin du tissu (Fig. 10) on suppose que le défaut apparaît surtout pendant le tissage et il ne peut pas être observe sur le tissu écru, mais sulement aprés des opérations d'ennoblissement.

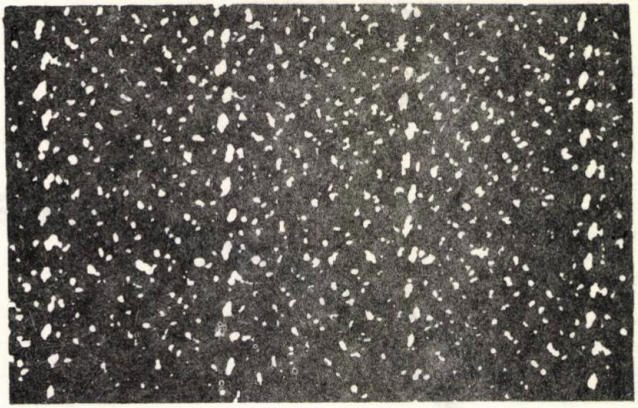

Fig. 2.– Bande blanchâtre (fils aplatis) sur un tissu à dessin.

Fig. 3.– Fibre simple en polyester qui présente des influences mécano-thermiques typiques de plastification et déformation.

Fig. 4.– Fibre simple en polyester (PES) qui prèsente des influences mécano-thermiques typiques de fusion du polymère.

Comme suite des défficiences qui apparaissent dans le processus de formation de la fibre, le ruban de polyester contient des fibres avec une structure fortement

Fig. 5.– Fibre en polyester à structure normale (couleur claire et fibre PES à grand contenu amorphe (couleur foncée) dégradée comme suite à une action thermo-mécanique.

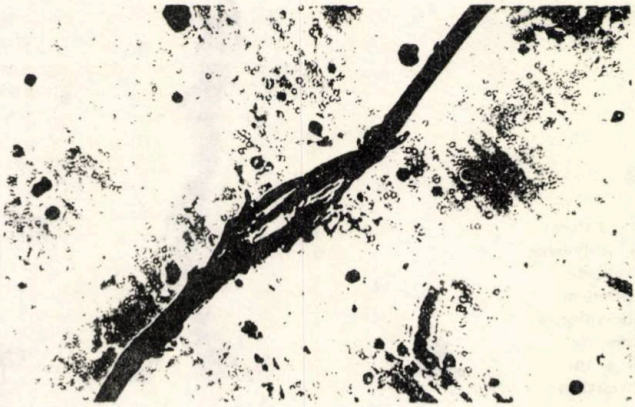

Fig. 6.– Fibre en polyester qui présente des influences mécano-thermique typiques d'écrasement.

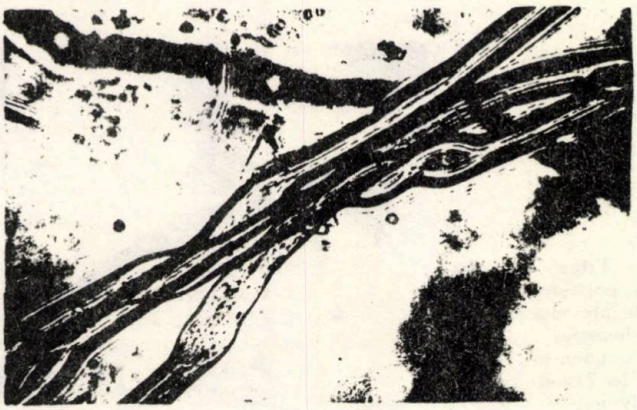

Fig. 7.– Fibres en polyester qui sous l'action mécano-thermique présentent des déformations locales.

amorphe ce qui confère à ces fibres de la rigidité et une résistance faible.

Dans ce cas les thermogrammes mettent en évidence une transition vitreuse entre 55-65°C caractéristique à un polymère amorphe dans la plus grande partie

Fig. 8.– Fibres en polyester dégradées du point de vue mécano-thermique avec la fusion du polymère.

Fig. 9.– Fibres en polyester qui présentent des déchirures et des adhérences à cause des influences mécano-thermiques.

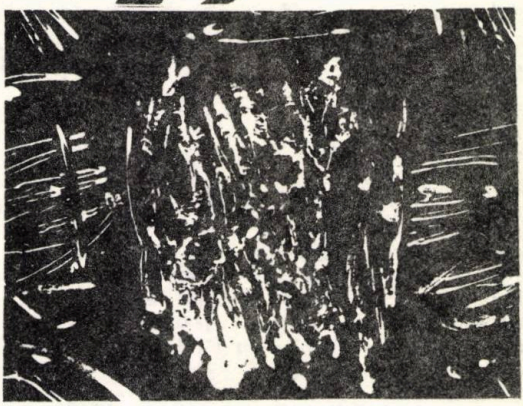

Fig. 10.– Fibres en polyester dégradées à la surface du fil.

(la température de vitrification de la normale est d'environ 78°C).

A cause du fait que ces fibres ont une thermostabilité faible elles se dégradent produisant des parties déformées des fibres qui, en contract avec les régions intactes donnent l'image de *plus clair* comme suite aux modifications de la reflexion de la lumière sur les régions détériorées.

4. Conclusions. Les causes possibles engendrent les défauts énoncés ci-dessus sur les métiers à tisser du type *Imatex* Târgu-Mureş peuvent être:

1. Dans la direction de la trame le défaut apparaît suite à des défficiences du mécanisme de lancement de la navette (la destruction du canal de protection du fil de la partie latérale de la navette, l'usure des lamelles du tablier de freinage du fil dans la navette, le centrage incorrect des ressorts de compression) ou au mécanisme de contrôle de la trame.

2. Dans la direction de la chaîne le défaut est dû à des défficiences au mécanisme de formation de la foule (la hauteur de la foule, le diagramme cyclique) et au mecanisme de contrôle du fil de chaîne.

Il faut remarquer le fait que dans les conditions des défficiences signalés ci-dessus, la thermodégradation a lieu surtout aux fibres à contenu amorphe élevé. Cela résulte clairement de la Fig. 5 óu on peut voir la détermination de la fibre colorée plus intensément qui a un contenu amorphe plus grand.

L'apparition des fibres aplaties sur le tissu peut être prévenue par:

1. L'avertissement des fabriques qui produisent des fibres en polyester relativement à l'apparition du défaut dans le tissu en vue du réglage approprié des paramètres des operations de filage et étirage.

2. Prêter plus d'attention aux réglages des outillages pour éviter les frottements locaux aux mécanismes suivants: le mécanisme de formation de la foule, le mécanisme de contrôle du fil de chaîne, le mécanisme de lancement de la navette, le mécanisme de contrôle de la trame.

3. Le remplacement à temps des sous-ensembles usés des mécanismes mentionnés ci-dessus.

4. Le maintien des paramètres du micro-climat de la section de tissage (l'humidité et la température de l'air) aux valeurs optimales durant toute l'année.

5. Le cirage des fibres avec des produits tensio-actifs appropriés à la composition fibreuse.

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CONTRIBUŢIE LA CUNOAŞTEREA FENOMENULUI DE APLATIZARE A FIRELOR ÎN PROCESUL DE ŢESERE

(Rezumat)

Se prezintă cauzele de natură structurală a fibrelor, precum şi deficienţele utilajelor ce contribuie la aplatizarea unor fibre din structura ţesăturilor tip lână pieptănată.

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Secţia VIII
TEXTILE. PIELĂRIE

ASPECTS CONCERNANT L'INFLUENCE DE L'HALOGÉNATION DES SUBSTRATS DE CAOUTCHOUC SUR L'ÉTALAGE DES LIQUIDES ADHÉSIFS

PAR
FLORENTINA HARNAGEA

1. Introduction. Dans l'industrie de chaussure on emploie une série de matériaux naturels et synthétiques, qui présentent des propriétés d'adhérence très différentes, fait qui exige hors l'emploi des adhésifs convenables aussi une préparation spéciale des substrats, qui conduisent à des adhérences augmentées.

D'après nos connaissances, pour l'augmentation de l'adhérence au cas des sistèmes formés de divers sortiments de caoutchouc comme substrat et des solutions à base des élastomères polyuréthaniques comme adhésifs, on utilise à bons résultats la méthode à chlorure des substrats de caoutchouc, comme sous le nom d'halogénation [1], [2], [3].

L'halogénation des substrats de caoutchouc a comme effet la modification de la tension superficielle qui contribue à la modification des processus d'etalage et de l'adhérence liquide–solide, aspect qui va se mettre en évidence dans ce travail ci présente.

2. Considérations théoriques. L'adhérence d'un produit pelliculogène sur la surface d'un matériel est, comme on sait, le résultat des forces intermoleculaires ou des interactions chimiques entre adhésif et substrat [2], [3]. Pour la manifestation de ces forces, il est nécessaire, parmi les autres, que l'adhésif soit un liquide à viscosité relativement petite, à capacité d'humectation du substrat et donc, s'étende sur le substrat en forme de pellicule.

Généralement, la capacité d'humectation de la surface solide par un liquide est appréciée par l'angle de contact dont la valeur est déterminée par la résultante de l'action des trois tensions superficielles: liquide–air (σ_{LA}), solide–liquide (σ_{SL}) et solide–air (σ_{SA}) (Fig. 1). La valeur de l'angle de contact par son cosinus constitue la mesure du degré d'humectation de la surface [4]:

$$\cos\theta = \frac{\sigma_{SA} - \sigma_{SL}}{\sigma_{LA}}$$

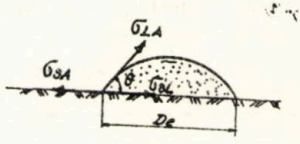

Fig. 1

Concernant les difficultés qui apparaissent à la mesure de cet angle dans le cas des liquides adhésifs, on pratique une methode indirecte d'appréciation de la capacité d'étalage d'un adhésif par la mesure du diamètre de la surface d'étalage (D_e) d'une goutte déposée sur le substrat [3], [4].

Un effet positif sur l'étalage et l'adhérence de l'adhésif polyuréthanique sur les substrats de caoutchouc népolaires le présente l'halogénation des surfaces avec des substances porteuses de chlore actif [1], [2], [3].

L'élément principal dans l'augmentation de l'adhérence le constitue le chlore actif, qui crée des centres puissamment polaires sur la surface du caoutchouc. Pour le traitement chimique des substrats de caoutchouc thérmoplastique et caoutchouc vulcanisé on emploie le mieux des agents d'halogénation à base d'acide trichlorisocianurique et on a essayé plus récemment l'utilisation des chloramines benzène sulfoniques [2], [3] qui par l'hidrolyse en milieu aqueux mettent en liberté du chlore et des amines convenables.

À présent on emploie un agent d'halogénation qui a à la base la dichloramine B, sous le nom d'Halogène H_1 – produit couramment à l'entreprise „Huşana". Tenant compte des choses mentionnées plus-haut, dans ce travail on présente une étude comparative entre Halogène H_1 et Icortin C 27R concernant la modification des propriétés superficielles des substrats de caoutchouc halogénés dans des conditions différentes.

3. La partie expérimentale. Pour mettre en évidence l'influence de l'halogénation des substrats sur l'étalage des adhésifs polyuréthaniques, on a utilisé la méthode de la mesure du diamètre de la surface d'étalage des gouttes de liquide adhésif de volume constant.

Dans ce but on a utilisé des divers matériaux avec lesquels les entreprises de chaussure travaillent couramment, à savoir: caoutchouc durocol, durolac, thermoplastique, lévicel, microporos M5, microporos M20. Les substrats de caoutchouc bien nettoyés ont été soumis à l'halogénation par brossage énergique des surfaces à l'aide d'un pinceau de PA. Après l'effacement avec l'agent d'halogénation des surfaces, on a attendu jusqu'à leur séchage, et l'aplication de l'adhésif a été faite à trente minutes depuis leur séchage.

Dans ce but on a utilisé un adhésif à base d'élastomères polyuréthaniques – Aderom 551. Les caractéristiques de l'adhésif et des agents d'halogénation sont présentées dans le Tableau 1.

Tableau 1

Adhésif polyuréthanique	Agent d'halogénation	
Adérom 551	Halogène H_1	Icortin C 27R
– concentration: 20,4% – viscosité à la coup Ford (ϕ = 8 mm): 70 sec. – résistence au détachement après 15 min – 4,0 N/mm après 72 h – 7,1 N/mm	– concentration: 4% – bicomponent à base de dichloramine B – temps minimum de séchage: 30 min.	– concentration: 2% – bicomponent à base d'acide trichlorisocianurique – temps minimum de séchage: 30 min.

Le sédiment des gouttes d'adhésif polyurethanique, de volume constant, s'est fait à l'aide d'une pompe d'injection sur la surface néhalogénées. À l'aide du microscope MM1 on a mesuré à une erreur de 0,01 mm, le diamètre d'étalage de la goutte comme moyenne de trois diamètres qui font entre eux, deux par deux, 45°.

La capacité d'humectation du liquide adhésif sur les substrats de caoutchouc présentés antérieurement, a été suivie à une heure, quatre heures, respectivement à vingt-quatre heures depuis la préparation de l'agent d'halogénation.

4. Résultats et discussions. Les résultats des mesures effectuées sur des substrats matériaux et sur des substrats traités avec les deux agents d'halogénation sont présentés dans le Tableau 2. Les augmentations des pourcentages du diamètre d'etalage en fonction de la nature des substrats traités à une heure, à quatre heures, respectivement à vingt-quatre heures depuis la préparation de l'agent d'halogénation sont envisagées en ordre de décroissance à l'aide des histogrammes dans la Fig. 2 pour Halogène H_1, et dans la Fig. 3 pour Icortin C 27R.

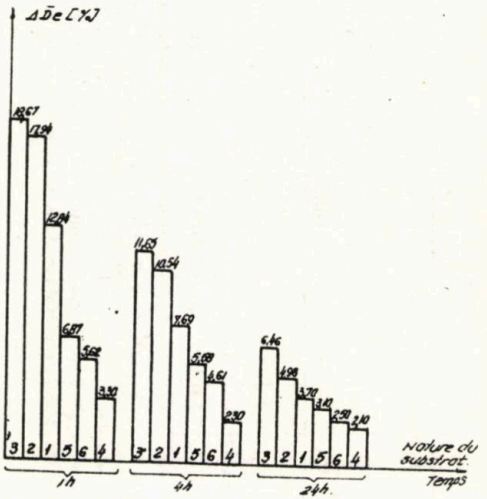

Fig. 2

Pour mieux poser en évidence la diminution de la capacité d'humectation des substrats traités dans des conditions différentes, dans la Fig. 4 on représente la variation du diamètre d'étalage en fonction du temps écoulé depuis la préparation de l'agent d'halogénation à l'application sur la surface des substrats de caoutchouc.

En analysant les valeurs des tableaux et les représentations graphiques, on constate les suivants:

– indiféremment de la nature des substrats aussi comme du temps écoulé depuis la préparation de l'agent d'halogénation à l'application sur le substrat, les valeurs moyennes du diamètre d'étalage sont plus grandes que dans le cas des substrats pas traités; les croissements pourcentageux sont compris entre 2 ... 19%;

– dans le cadre des trois temps divers après quoi on a réalisé l'halogénation des substrats, les meilleures valeurs ont été obtenues au traitement par l'effacement

Tableau 2

La nature du substrat	Des substrats néhalogénés	Substrats halogénés avec Halogène H_1									Substrats halogénés avec Icortin C 27R								
		$t = 1$ h			$t = 4$ h			$t = 24$ h			$t = 1$ h			$t = 4$ h			$t = 24$ h		
	$\overline{D}_e$	$\overline{D}_e$	$\Delta\overline{D}_e$		$\overline{D}_e$	$\Delta\overline{D}_e$		$\overline{D}_e$	$\Delta\overline{D}_e$		$\overline{D}_e$	$\Delta\overline{D}_e$		$\overline{D}_e$	$\Delta\overline{D}_e$		$\overline{D}_e$	$\Delta\overline{D}_e$	
			mm	%		mm	%		mm	%		mm	%		mm	%		mm	%
1.	7,02	7,93	0,91	12,84	7,56	0,54	7,69	7,28	0,26	3,70	7,91	0,89	12,74	7,49	0,47	6,69	7,26	0,24	3,43
2.	7,02	8,28	1,26	17,94	7,76	0,74	10,54	7,37	0,35	4,98	8,08	1,06	15,09	7,64	0,62	8,92	7,31	0,29	4,08
3.	7,12	8,53	1,41	18,67	7,95	0,83	11,65	7,58	0,46	6,46	8,30	1,18	16,58	7,81	0,69	10,20	7,54	0,42	5,92
4.	6,98	7,21	0,23	3,30	7,14	0,16	2,30	7,13	0,15	2,10	7,19	0,21	3,00	7,13	0,15	2,20	7,12	0,14	2,00
5.	6,98	7,46	0,48	6,87	7,37	0,39	5,58	7,20	0,22	3,10	7,42	0,44	6,31	7,28	0,30	4,35	7,19	0,21	3,00
6.	6,93	7,32	0,39	5,62	7,25	0,32	4,61	7,11	0,18	2,59	7,28	0,35	5,02	7,21	0,28	4,04	7,10	0,17	2,45

Notations: 1. – caoutchouc durolac; 2. – caoutchouc durocol; 3. – caoutchouc thermoplastique; 4. – caoutchouc lévicel; 5. – caoutchouc microporos type 5; 6. – caoutchouc microporos type 20; $\overline{D}_e$ – valeur moyenne du diamètre d'étalage; $\Delta\overline{D}_e$ – l'accroissement du diamètre d'étalage dans la valeur absolue et en pourcentage envers le diamètre d'étalage du substrat néhalogéné.

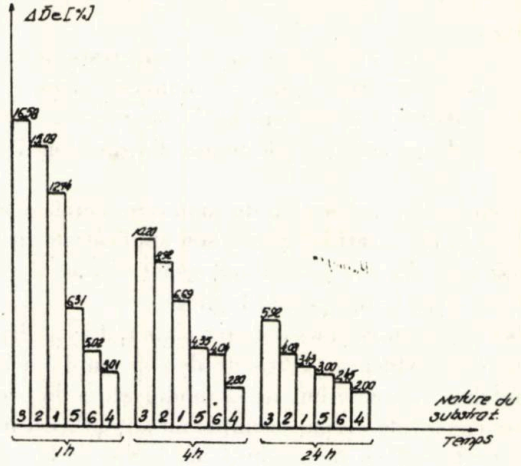

Fig. 3

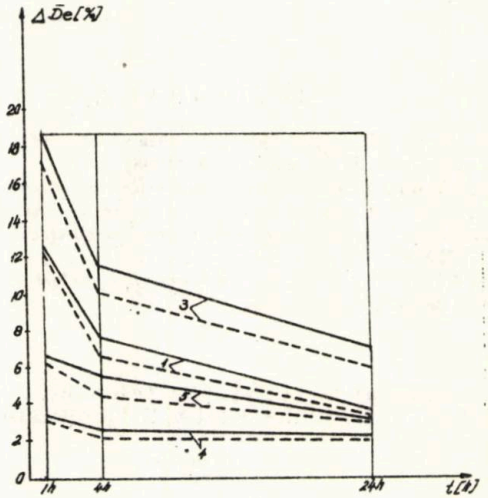

Fig. 4

des surfaces à une heure depui le mélange des deux composants (solide et liquide) de l'agent d'halogénation, bien que dans la littérature de spécialité on recommande l'utilisation pendant 24 heures depuis la préparation;

– la diminution en temps du diamètre d'étalage, respectivement de la capacité d'humectation, met en évidence le fait que le processus de décomposition de l'agent d'halogénation commence depuis la phase solvable; cette diminution étant plus puissante aux substrats de caoutchouc thermoplastique, durocol et durolac;

– l'efficacité de l'agent d'halogénation Halogène H_1 est plus grande on près de celle de l'agent d'halogénation Icortin C 27R, fait pour lequel on recommande son utilisation dans toutes les entreprises de chaussure.

5. Conclusions.

a) L'effet positif de l'halogénation des substrats de caoutchouc, utilisés à la réalisation des dates expérimentales, se manifeste dans le processus de l'étalage des liquides adhésifs par l'accroissement du diamètre de la surface d'étalage, fonction de la nature des substrats et le temps d'utilisation de l'agent d'halogénation bicomposant.

b) Ayant en vue le diminution du diamètre d'étalage en fonction de la durée du temps depuis la préparation jusqu'à son application sur la surface du substrat, on recommande l'emploi de l'agent d'halogénation plus vite après la dissolution du composant solide dans le composant liquide.

c) Les résultats comparables obtenus pour Halogène H_1 (par rapport à Icortin C 27R) mettent en évidence l'efficacité de son emploi à l'halogénation des substrats de caoutchouc dans le but de la modification du processus d'étalage et de l'adhérence liquide–solide. Tenant compte du fait qu'il est moins toxique en résulte que son emploi est meilleur même du point de vue de la protection du travail.

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ASPECTE PRIVIND INFLUENŢA HALOGENĂRII SUBSTRATURILOR DE CAUCIUC ASUPRA ETALĂRII LICHIDELOR ADEZIVE

(Rezumat)

Se prezintă eficacitatea agentului de halogenare *Halogen* H_1 – pe bază de Dicloramină B –, comparativ cu *Icortin* C 27R, asupra capacităţii de umectare a adezivului poliuretanic pe suprafaţa substraturilor de cauciuc, halogenate la intervale de timp diferite de la prepararea agentului de halogenare bicomponent.

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Secţia VIII
TEXTILE. PIELĂRIE

PROJECTION ASSISTÉE PAR ORDINATEUR DES MOULES POUR CONTREFORTS DE CHAUSSURE

PAR
CORNELIA IONESCU et FLORENTINA HARNAGEA

1. Introduction. Le formage des contreforts de chaussure est réalisé dans des moules composés d'un noyau, de deux pièces latérales de fermeture et d'une pièce qui ferme la zone active du noyau (Fig.1).

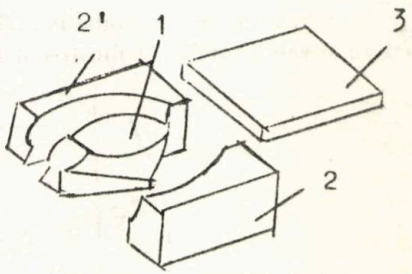

Fig. 1.– *1* – noyau; *2,2',3* – pièces de fermeture.

Le noyau du moule constitue la pièce de base qui détermine la forme spatiale du contrefort. Il comporte 2 zones, l'une active, sur laquelle se forme le contrefort et l'autre, inactive, qui contribue à fixer le contrefort sur la machine.

Les matières utilisées pour contreforts présentent, pendant le formage, un comportement élasto-plastique, caracterisé par un indice de formage dont la valeur est déterminée expérimentalement [1].

À la base de la projection du noyau se trouve le conformateur sur lequel sera modelée la chausure à contrefort spatialisé dans le moule.

Le passage du contour de la forme au contour de la zone active du noyau du mole repose sur une méthode géométrique de projection qui tient compte de l'indice de formage de la matière utilisée.

2. Projection géométrique de la zone active du noyau de mole. Dans ce processus on parcourt les étapes suivantes [2]:

– obtention des sections du conformateur dans les 3 plans;

– modification des sections du conformateur par application de l'indice de formage;

– corrélation des sections modifiées dans les 3 plans.

Les contours des sections copiés sur le conformateur se composent d'une succession d'arcs de cercle dont les rayons et les angles au centre sont différents (Fig.2).

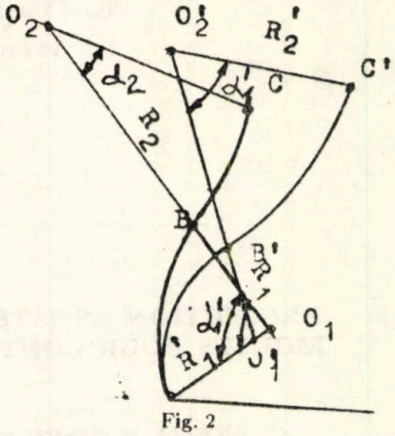

Fig. 2

En appliquant l'indice de formage on obtient les contours de la zone active du noyau du moule par les relations [3]:

$$R_i' = R_i If \qquad (1)$$

$$\alpha_i' = \frac{\alpha_i}{If} \qquad (2)$$

où: R_i' – longueur des rayons des arcs de cercle appartenant au contour du conformateur; R_i – longueur des rayons des arcs de cercle appartenant au noyau du moule; α_i – angles au centre des arcs de cercle sur le conformateur; α_i' – angles au centre des arcs sur le noyau de moule; If – indice de formage de la matière utilisée pour contreforts.

La corrélation des contours modifiés du conformateur qui conduit au contour final du noyau du mole est illustrée dans la Fig.3.

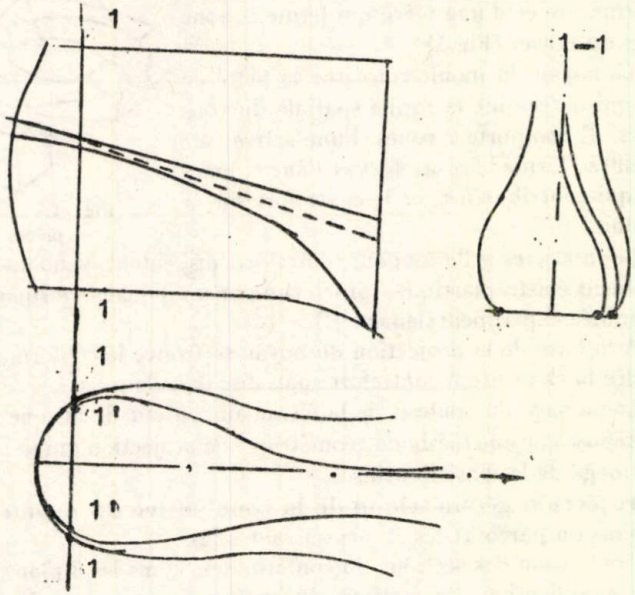

Fig. 3

L'identification des arcs de cercle, la détermination des valeurs des rayons et des angles pour tous les contours copiés sur le conformateur et des opérations de modification et de corrélation de ces contours qu'on effectue pour obtenir le noyau

du moule par la méthode géométrique, sont laborieuses et permettent l'apparition de certaines erreurs. Ces inconvénients peuvent être éliminés par la projection assistée par ordinateur.

3. Algorithmes utilisés pour la projection de la zone active du noyau du moule pour contrefort. La modification de tous les contours du conformateur est efectuée d'après le même schéma de principe.

Procédure CALCULS

En considérant l'exemple général de la Fig.4, on identifie dans la structure de l'algorithme les indicateurs et les variables suivants: n – indicateur à 2 valeurs: $ind = 1$ pour le contour réel; $ind = 2$ pour le contour modifié; j – indicateur à 2 valeurs: $j = 1$ pour le contour du côté gauche; $j = 2$ pour le contour du côté droit; i – nombre des arcs de cercle pour un contour; $nc(j)$ – nombre des arcs de cercle pour chacun de nouveaux contours modifiés; $m(n, j, i)$ – indicateur pour les zones concaves et convexes d'un contour: $m(ind, j, i) = 1$ pour les zones concave; $m(ind, j, i) = -1$ pour les zones convexes; $r(n, j, i)$ – matrice tridimensionnelle qui mémorise les valeurs propres à chaque rayon tant pour le contour initial que pour le contour modifié; $cx(n, j, i)$; $cy(n, j, i)$ – matrice tridimensionnelle qui mémorise les valeurs propres aux centres des arcs de cercle tant pour le contour réel que pour le contour modifié; $mi(n, j, i)$; $ma(n, j, i)$ – matrice qui mémorise les valeurs de l'angle initial et de l'angle final des rayons polaires; $fi(n, j, i)$ – angle du rayon polaire à l'axe ox; $u(a, j, i)$ – valeurs initiales des angles de cercle résultés de la décomposition du contour réel.

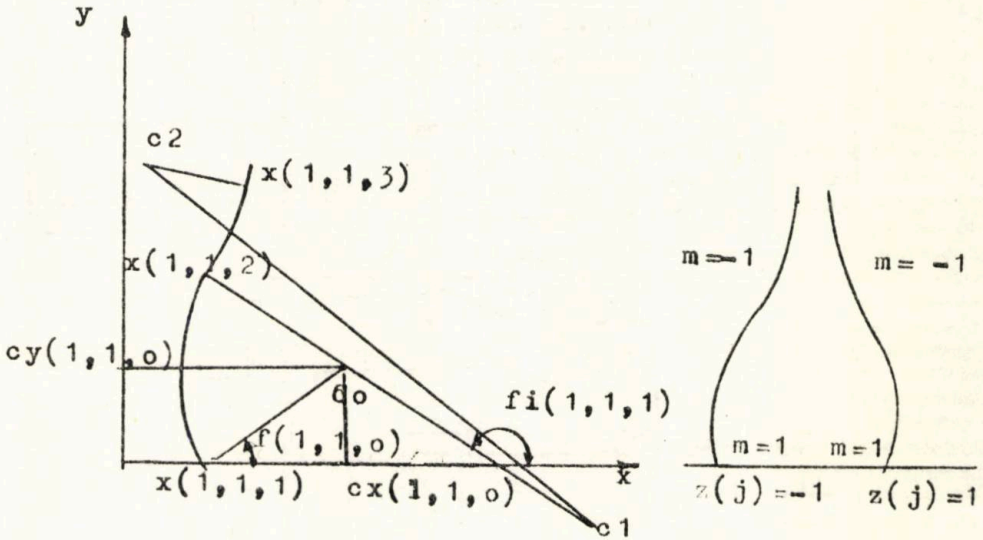

Fig. 4

La procédure CALCULS présentée aura comme valeurs de sortie les valeurs des centres des arcs de cercle du contour modifié, $cx(n, j, i)$; $cy(n, j, i)$ et les valeurs des

coordonnées finals de chaque arc de cercle du contour modifié, $x(n,j,i)$, $y(n,j,i)$.

Le schéma logique pour la procédure CALCULS est présenté dans la Fig.5.

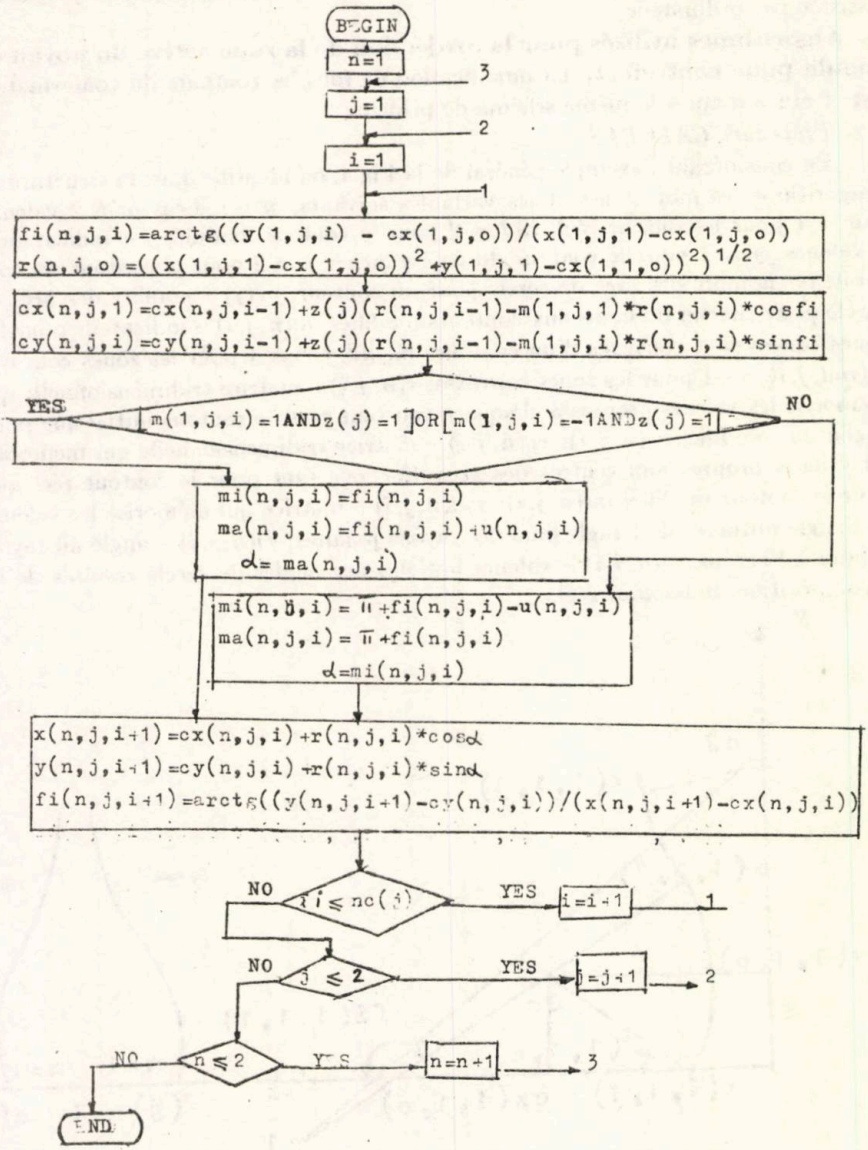

Fig. 5.– Schéma logique pour la procédure CALCULS.

Procédures CORECT1 et CORECT2

Ces procédures fournissent à la procédure graphique les valeurs nécessaires à la translation du contour modifié du côté droit, corespondant à la section transversale, avec une valeur résultée de la modification de la section transversale par rapport à l'axe du contour de la surface plantaire.

Le rôle de la procédure CORECT1 est de calculer la distance, mesurée sur le contour réel, entre le point d'origine et le point qui définit la position de la section transversale sur le contour de la surface plantaire de la forme (Fig.6).

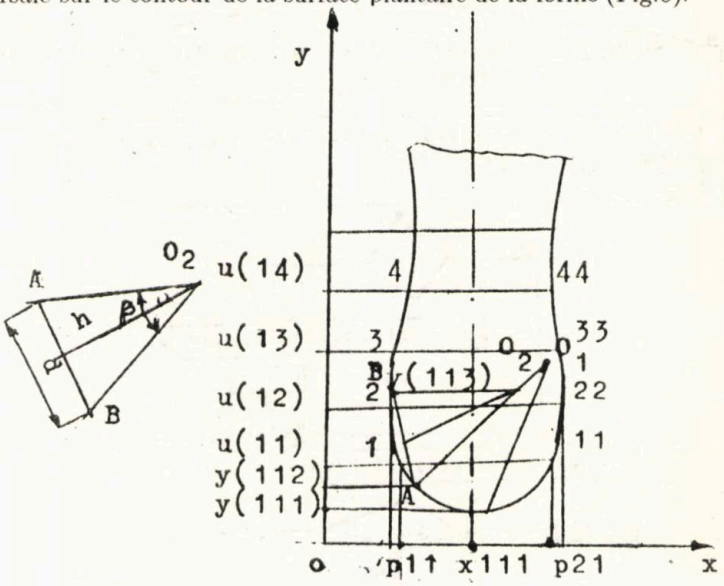

Fig. 6

Les valeurs d'entrée de la procédure CORECT1 sont: ns – nombre des sections transversales; ln – variable qui mémorise les longueurs des arcs de cercle pour lesquelles on effectue le calcul; $lg(1,j,k)$ – matrice qui mémorise les valeurs des longueurs définies antérieurement; $r(1,j,l)$; $u(1,j,l)$; $y(n,j,i)$; $x(n,j,i)$ – dont les significations sont définies dans la procedure CALCULS.

Les valeurs d, h, β ont les significations de la Fig.6.

La procédure CORECT2 utilise comme valeurs d'entrée les valeurs de l'indice $lg(1,j,i)$, valeurs de sortie dans les procedure CORECT1 et fournit comme valeurs de sortie les vecteurs $xp(2,j,k)$ et $yp(2,j,k)$ où sont mémorisées les coordonnées des points de base sections transversales modifiées.

Les valeurs d'entrée de la procédure CORECT2 sont: r_1, r_2 – longuers entre lesquelles se situe la valeur de $lg(1,j,i)$ dans une itération; lf – variable nécessaire à exprimer les longueurs des arcs de cercle additionnées, dont la valeur est inférieure à celle de $lg(1,j,i)$; $\gamma(2,j,k)$ – angle dont la valeur est inférieure a celle de $u(2,j,i)$ correspondant à la position de la section transversale sur le contour modifie.

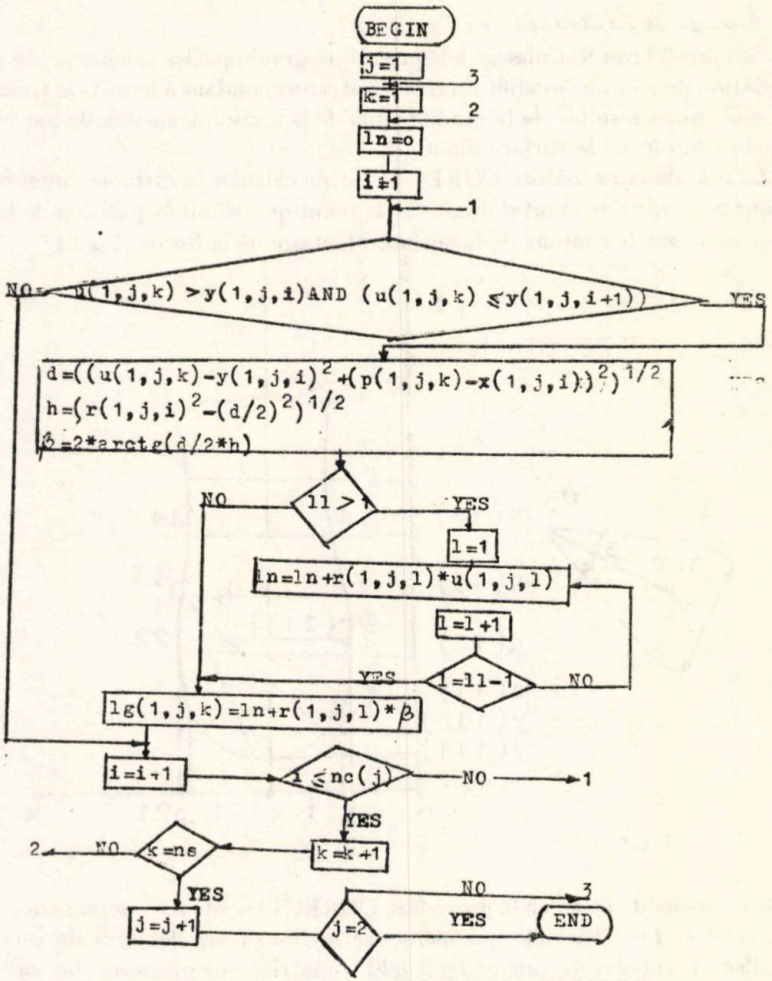

Fig. 7.– Schéma logique pour la procédure CORECT1.

Les valeurs de sortie sont: les coordonnées $xp(2, j, i)$ et $yp(2, j, i)$ qui définissent l'intersection des sections transversales avec le contour de la surface plantaire.

Les schémas logiques pour les procédures CORECT1 et CORECT2 sont présentés dans la Fig.7 et la Fig.8.

Le schéma logique finale est présenté dans la Fig.9.

L'application sur ordinateur a été réalisée en langage Turbo-Pascal.

Les algorithmes établis peuvent être appliqués pour la modification de n'importe quelle forme de la forme.

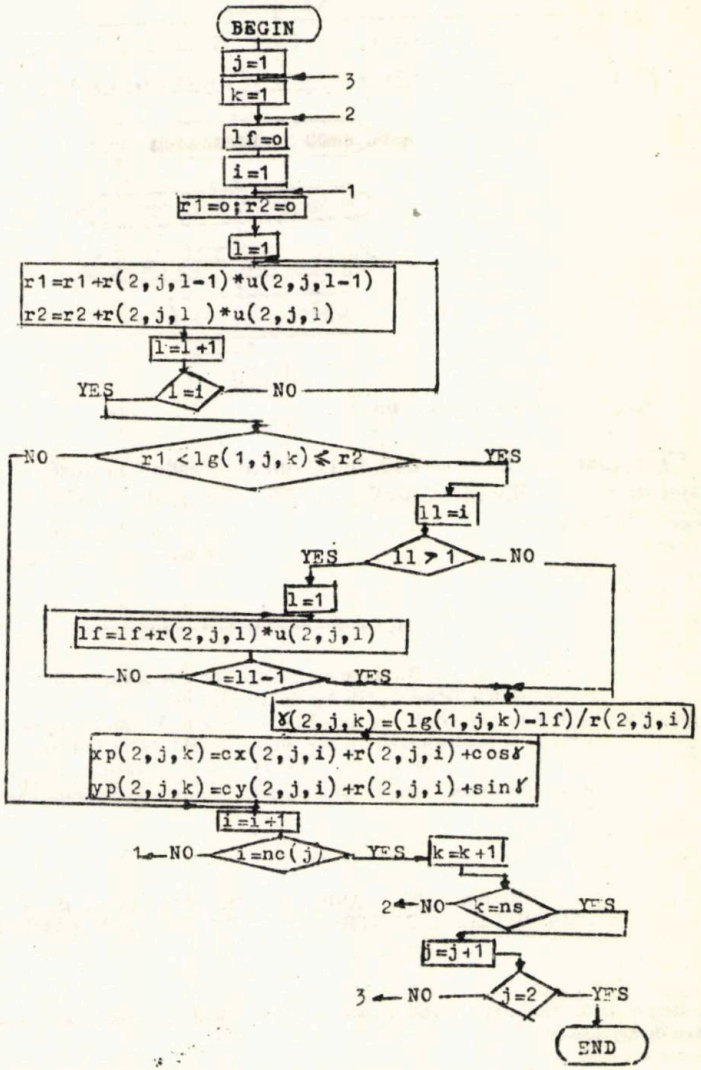

Fig. 8.– Schéma logique pour la procédure CORECT2.

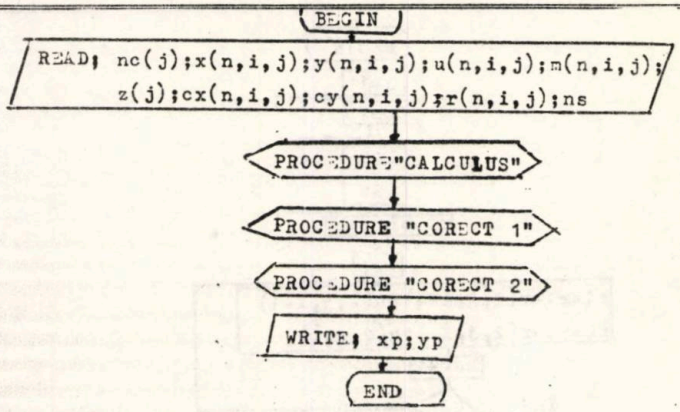

Fig. 9.– Schéma logique finale

4. Conclusions. L'utilisation de l'ordinateur réduit la durée de l'élaboration du projet de 80% et élimine complètement les erreurs de la méthode géométrique.

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PROIECTAREA ASISTATĂ DE CALCULATOR A MATRIŢELOR PENTRU ŞTAIFURI DE ÎNCĂLŢĂMINTE

(Rezumat)

Se prezintă o metodă de proiectare asistată de calculator a matriţelor pentru format ştaifuri pentru încălţăminte.

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Secţia VIII
TEXTILE. PIELĂRIE

ÉTUDES CONCERNANT L'UTILISATION RATIONNELLE DE LA MATIÈRE À LA FABRICATION DES CHAUSSURES

PAR
MARIANA COCEA, GABRIELA MĂLUREANU,
FLORENTINA HARNAGEA et CODRINA RĂDĂVOI

1. Introduction. L'objectif central de l'activité économique développée dans les societés qui produisent des chaussure dans les conditions concurrentielles de marché est constitué par la fabrication des produits de qualité ayant des prix minimaux pour les producteurs mais aussi pour les bénéficiaires.

Une analyse sommaire de la situation actuelle met en évidence une dotation technique précaire à celle des fabricants similaires des chaussures des pays à potentiel technique et économique élevé (L'Allemagne, Amérique, l'Italie etc.), ce qui diminue dés le commencement des chances d'existence dans le mécanisme concurrentiel de l'économie de marché.

Le fabricant de chaussure doit devenir toujours plus conscient de la nécessité du passage des systèmes du travail manuel ou des systèmes manuels et mécaniques, utilisés à présent, des modifications bénéfiques pendant les étapes technologiques.

Ayant en vue les avantages particuliers de l'utilisation des systèmes de calcul il y a dans le monde des centres de projection des chassures qui permettent à chaque produit, à partir de la forme et de la dimension de l'embauchoir l'obtention de la copie moyenne et le contour des repères aussi que les formes planes des repères sous la forme des patrons de projection et d'exécution.

La conjuncture économique actuelle rend impossible pour la majorité des fabricants des chaussures roumains le grand effort financier imposé par l'automatisation dans une seule étape des processus de fabrication par l'acquisition des programmes et des installations des producteurs reconnus dans le monde entier.

Dans ce sens on a considéré comme prioritaire à cette étape l'automatisation de quelques phases du processus de préparation de la fabrication tenant compte des implications majeures dans la réalisation des effets positifs tout le long du flux de fabrication des chaussures, ce qui constitue le sujet du thème de recherche proposée.

Cela permet la realisation rapide des gammes multiples de produits, l'exécution rapide de l'operation de graduation, la réduction des consommations spécifiques dans les conditions de l'amélioration des variantes d'encadrement, l'obtention des

données qui fassent possible l'automatisation des opérations du processus de fabrication à mesure qu'on aquiert des installations automatiques de coupe, des machines automatiques à coudre etc.

On vient de préciser dans les étapes antérieurs du thème de recherche proposée que dans la technologie actuelle de préparation de la fabrication l'élaboration de la documentation technique d'un produit de chaussure comprend une série d'activités particulièrement laborieuses ayant un certain degrés de routine comme: le détail du dessin de base en vue de la définition, de la configuration des patrons, la détermination des aires des repères et de la longueur de leur contour, pour estimer les consommations des matériaux et des auxiliaires (peaudessous, peau doublures, matériaux textiles).

La prise des décisions concernant le choix de la variante de l'arrangement des repères sur la surfaces du matérial à la coupe des repères, le choix de la variante du processus de l'usinage-assemblage rest, le plus souvent, une action influencée fréquemment par le subjectivisme de l'exécutant ou du technicien du processus ayant en vue le temps réduit de la prise de décision concernant ce probleme.

Les repères composant les produits en cuir ont des configuration très différentes au cadre du méme produit, mais aussi d'un produit à l'autre dans les conditions de la distinctions sous le rapport des divers critères (peinture, largeur, destination).

La définition de la configuration de ces contours, a l'étape de la projection constructive, dans les conditions imposées par la diversité des gammes toujours plus accentuées doit être faite dans l'acception des consommation minimales de matière première et de la main-d'oeuvre [1], [2].

Cela implique la détermination, pour toutes les variantes constructives conçues des produits, de l'aire des repères, de leur périmètre en vue de la prise de décisions sur certaines variantes constructives optimisées sous rapport des consommations des matériaux et de la main-d'oeuvre.

La principale difficulté de cette activité est le contour irrégulier des repères qui doit être précisé par l'intermédiaire d'un numéro correspondant de points caractéristiques, dont la position s'établit selon leur aspect irrégulier [3], [4].

La forme irrégulière des contours de ces repères rend plus difficiles aussi certaines activités technologiques du processus de confectionnement comme, par exemple, l'établissement d'encadrements qui assurent une consommation minimale de matériaux a l'exécution des certains usinages selon le contour.

Au sein de la collectivité de recherche-projection confection en cuir de la Faculté de Textiles-Cuir on a élaboré un produit soft pour le modelage mathématique d'un contour irrégulier à „spline" fonctions, le calcul de l'aire et du périmètre du contour, la création d'une interface de travail avec ACAD pour obtenir a l'échelle réelle le repère.

Tenant compte que le cout de production d'un produit de chaussure est de plus de 65% du cout de la matière première, à l'intérieur de ce travail on a fait des études concernant:

– la projection économique des repères des produits de chaussure et de maroquinerie;

– l'emploie rationnel de la surface des matériaux.

Tenant compte des résultats obtenus le long de ce travail, on a insisté sur la modalité d'utiliser rationnellement les peaux à la coupe, ayant en vue les facteurs suivants:

– l'aire de la superficie et le contour de la peau;

– le contour des repères;

– le rapport de dimension entre les aires des repères d'un produit, aussi que le rapport entre l'aire de la superficie du matériau et des repères;

– des restrictions envisageant la position des repères sur la superficie du matériau au débit.

Quant à ce probleme, il a fallu faire des études concernant les systèmes des rangement des repères des dessous à la coupe des peaux pour obtenir un facteur de position qui conduise aux normes de consommations minimales.

Pour obtenir un produit soft qui permette l'utilisation rationnelle du matériau à la coupe, en connaissant les facteurs déja mentionnés, on a fait appel aux possibilités offertes par la géométrie analytique, differentielle, sur les transformations géométriques dans différents systèmes de coordonnées dans l'espace 2D [5].

À partir de ces études on a élaboré des sous-routines pour:

– le passage d'un système de coordonnées à un autre;

– des scalaires dans le système de coordonnées imposé;

– des translations;

– des rotations;

– des multiplications.

Dans ce travail on présente trois modèles de chaussure type „soulier garçons", pour lesquels on a calculé la norme de consommation et le rendement d'utilisation avec le produit soft presenté pour établir le produit de chaussure qui pourrait constituer l'objet d'une production en série [6].

2. La présentation du produit. Pour l'étude des normes de consommation on a diversifié un modèle de chaussure (modèle 001) en trois modèles constructives (modèle 002, 003), représentées dans la Fig.1.

L'article projeté se caracterise par les restrictions suivantes:

– le genre de chaussure	– souliers
– destination	– garçons
– système de confection	– IL
– le groupe du produit	– EXTRA
– la pointure de l'embauchoir	– 20,5 mm
– la hauteur du talon	– 15 mm
– la longueur de la copie moyenne	– 230 mm
– principaux matériaux	– dessous – peaux bovines f.n.
	– doublures – croutre, velour
	– semelle moyenne – caoutchouc compact

Le modèle est fabriqué dans la variante tige au-dessus de l'empeigne.

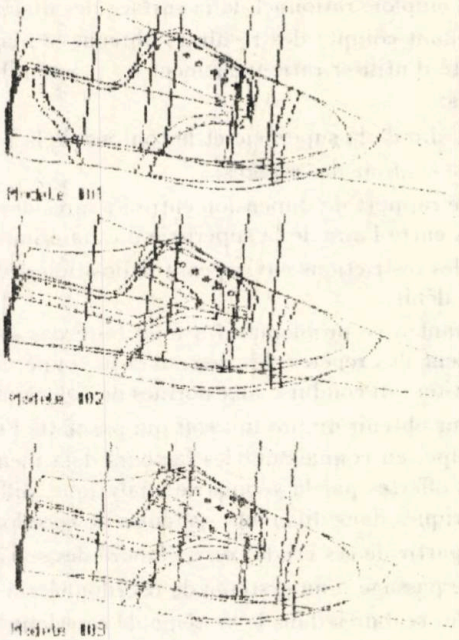

Fig. 1

3. L'élaboration des modèles théoriques et pratiques d'encadrement. L'établissement des éléments primaires de calcul, des normes estimatives de consommation pour différents types de matériaux.

Le modèle de rangement théorique est la variante de rangement représentée par la translation linéaire des repères avec ou sans rotation sur les filles. Au cas où on considere que la superficie est sans fin et on met cette variante répétable sur la superficie du matériau tout entiére, entre les repères il y a des pertes grace au fait qu'il y a seulement des points des tangence entre les repères.

En reliant les mêmes points sur 4 repères on ferme un parallélogramme a l'intérieur duquel il y a un nombre entier de repères, en pieces (Fig.2).

On calcule le facteur de rangement avec la formule:

$$F_a = n\frac{s_n}{s_p},$$

où: n – le numéro de repères complets de l'intérieur du parallélogramme; s_n – la superficie utile, la superficie du parallélogramme; s_p – la superficie utile, planimétrée d'un repère.

Les pertes qui paraissent pendant le processus de la coupe au moment du rangement du même repère sur la superficie du matériau sont influencées par la configuration du contour, mais aussi par la variante de rangement adoptée.

Les rangements théoriques des trois modèles étudiés en vue de l'établissement de la variante la plus avantageuse du point de vue du producteur et de celui de

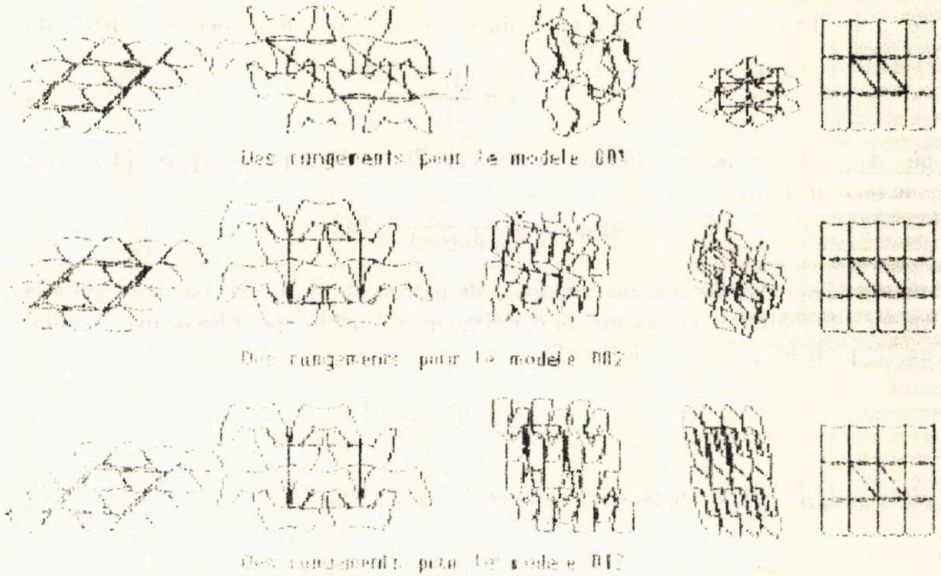

Fig. 2

l'acheteur sont représentées dans la Fig.2.

Pour le calcul des normes de consomation on utilise les relations:

$$A_{DN} = A_{ps} - A_s \quad [\text{dm}^2],$$

où: A_{DN} – l'aire des déchets normés grace a la configuration courbe des repères [dm^2]; A_{ps} – l'aire du parallélogramme du set [dm^2]; A_s – l'aire du set;

$$a_{DN} = \frac{A_{DN}}{A_s} 100 \quad [\%],$$

où: a_{DN} – l'aire des déchets normés [%];

$$A_{DP} = p\frac{P_s}{2} \quad [\text{dm}^2],$$

où: A_{DP} – l'aire des déchets normés [%]; p – la dimension du pont [dm]; P_s – le périmètre du set [dm];

$$a_{DP} = \frac{A_{DP}}{A_s} 100 \quad [\%],$$

où: a_{DP} – l'aire des déchets par ponts;

$$A_S = \frac{A_S}{m_S} \quad [\text{dm}^2],$$

où: A_S – l'aire moyenne des repères du set [dm^2]; m_S – le numéro de repères du set;

$$F_A = \frac{A_{PL}}{A_S},$$

où: A_{PL} – l'aire moyenne de la peau de laquelle on découpe les repères [dm^2]; F_A – le facteur d'aire;

$$a_{Dm+Dt} = \frac{a}{(FA)^{1/4}}, \quad [\%],$$

où: a_{Dm+Dt} – les déchets marginaux et de patron [dm^2]; a – la constante qui a la valeur différente selon la nature du matériau qui est débité (pour les peaux flexibles, a=39; pour les peaux rigides, a=25);

$$A_{Dm+Dt} = \frac{a_{Dm+Dt}A}{100},$$

où: A_{Dm+Dt} – les déchets marginaux et de patron [dm^2];

$$A_{DT} = A_{DN} + A_{DP} + A_{Dm+Dt},$$

où: A_{DT} – l'aire des déchets totaux;

$$N_C = (A_S + A_{DT})I_C,$$

où: I_C – l'indice de qualité (pour les quatre qualités, I_C est: I, I_C=0,97; II, I_C=1; III, I_C=1,03; IV, I_C=1,1).

Au cas des peaux rigides on donne en unités de masse, et aux peaux flexibles, en unités d'aire, donc:

$$N_C = A_S\left(1 + \frac{a_{DT}}{100}\right)I_C,$$

où: N_C – la norme de consommation [%];

$$U = \frac{100A_S}{N}, \quad [\%],$$

où: U – le rendement de l'utilisation de la peau.

Le rendement d'utilisation de la peau sera calculé seulement pour la deuxième qualité (I_C=1). Pour l'indice on a accepté l'idée que les défauts de la superficie de la peau seront inclus sur la surface des déchets normaux, entre les patrons, les marginales où par les ponts.

Pour le calcul des normes de consommation et du rendement de l'utilisation on a élaboré un programme sur un ordinateur IBM-PC dont les résultats sont présentés dans le Tableau 1.

Tableau 1

Le calcul des normes de consommation et du rendement d'utilisation pour:

Modèle no. 001

Ar_{rep}	Nr_{rep}	Pr_{rep}	Ap
.57930E+00	.20000E+01	.30580E+01	.12612E+01
.11429E+01	.20000E+01	.56750E+01	.33744E+01
.86580E+00	.40000E+01	.42060E+01	.39000E+01
.43810E+00	.20000E+01	.36900E+01	.10352E+01
.32240E+00	.20000E+01	.23340E+01	.68440E+00

L'aire des déchets totaux: .31116E+01, .36917E+02; la norme de consommation: .11194E+02, .11540E+02, .11886E+02, .12694E+02; le rendement d'utilisation: .75296E+02, .73037E+02, .70910E+02, .66397E+02; le rendement moyen d'utilisation: .71141E+02.

Modèle no. 002

Ar_{rep}	Nr_{rep}	Pr_{rep}	Ap
.16021E+01	.20000E+01	.60310E+01	.38829E+01
.75570E+00	.40000E+01	.40900E+01	.35372E+01
.67490E+00	.20000E+01	.44350E+01	.15256E+01
.32240E+00	.20000E+01	.23340E+01	.68440E+00

L'aire des déchets totaux: .26617E+01, .32374E+02; la norme de consommation: .10557E+02, .10883E+02, .11210E+02, .11972E+02; le rendement d'utilisation: .77880E+02, .75543E+02, .73343E+02, .68676E+02; le rendement moyen d'utilisation: .73861E+02.

Modèle no. 003

Ar_{rep}	Nr_{rep}	Pr_{rep}	Ap
.57930E+00	.20000E+01	.30580E+01	.12611E+01
.12902E+01	.20000E+01	.61000E+01	.34304E+01
.77170E+00	.40000E+01	.53110E+01	.37138E+01
.29590E+00	.40000E+01	.30020E+01	.12916E+01
.32240E+00	.20000E+01	.23340E+01	.68440E+00

L'aire des déchets totaux: .31065E+01, .35896E+02; la norme de consommation: .11408E+02, .11761E+02, .12114E+02, .12937E+02; le rendement d'utilisation: .75862E+02, .73586E+02, .71442E+02, .66896E+02; le rendement moyen d'utilisation: .71946E+02.

Ar_{rep} – l'aire des repères; Nr_{rep} – nombre de repères; Pr_{rep} – périmètres des repères; Ap – l'aire du parallélogramme.

4. Conclusions. Pour obtenir, à l'aide de la technique de calcul, une configuration des repères d'un produit, la détermination des paramètres géométriques principaux, l'établissement des encadrement d'un patron où des patrons sur un matériau, l'execution de certains usinage selon le contour, la réglementation des consommations de matériau sont des opérations absolument nécessaires pour élever l'efficience de l'activité de l'agent économique, fabricant de chaussure.

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STUDII PRIVIND UTILIZAREA RAŢIONALĂ A MATERIEI PRIME LA FABRICAREA ÎNCĂLŢĂMINTEI

(Rezumat)

S-a efectuat un studiu privind utilizarea raţională a materiei prime în industria confecţiilor din piele. În acest scop s-a proiectat, cu ajutorul calculatorului, un model de încălţăminte „pantof băieţi", care s-a diversificat în alte cinci modele, în vederea stabilirii variantei celei mai convenabile din punct de vedere economic. În lucrare sunt prezentate trei modele, pentru care s-a studiat consumul de materie primă necesară pentru realizarea ansamblului superior.

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Tomul XLI (XLV), Fasc. 1–2, 1995
Secţia VIII
TEXTILE. PIELĂRIE

CONTRIBUTIONS TO A MATHEMATIC MODELLING OF ADHESION PROCESSES IN FOOTWEAR INDUSTRY

BY
AURA MIHAI

1. Introductory Notions. The question of correct dimensioning of a joint by adhesion is imposed by the conditions in which the predominance of the AF (Adhered Footwear) system is more and more used in the footwear industry. On the other hand, the same aspects related to the joint between the upper and lower parte may be met with in the case of other two systems of leather industry with a large use in the field: Cured Footwear (CF) and Injected Footwear (IF).

The direct dimensioning of a joint by means of adhesion supposes the avoidance of the two extremes: super- and sub-dimensioning. In this way along the whole process of adhesion we are interested in getting ballanced joints where an eventual rupture should not occur dued to the following five variants (Fig. 1):

– joint rupture in one of the two sublayers;

– joint rupture in one of the two contact surfaces;

– joint rupture within the film.

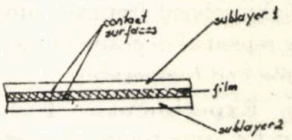


Fig. 1

In order to get to this ideal situation as to a correct dimensioning of a joint, we have to know every parameters that might influence such a process, parameters that may be grouped into three main categories:

a) parameters related to the features of the solid material;

b) parameters related to the features of filmogeneous substance;

c) parameters related to the technology of adhesion.

a) *Parameters related to the features of the solid material.* Generally the solid surfaces have not a smooth surface. In the practice of adhesion they resort even to create certain unregularities through which besides an increased contact surface solid-film, a stranger anchorage of the film to the sublayer and the coat, and of the sublayer to the film is also provided.

This phenomenon might be described by means of a formula:

$$A = a_{1-2} \cdot S_g \cdot Cs,$$

where: A – adherence between the film and the support; a_{1-2} – specific adhesion; S_g – geometrical area of the surface; Cs – the coefficient of the specific surface.

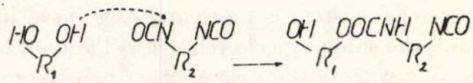
Each parameter may influence more or less the ample process of adhesion. In regular practice they use to perform an operation of linting the drawing reserve with abrasive paper of various granulations, modifying in this way the coefficient of the specific surface.

b) *Parameters related to the features of the filmogenous substances.* In their turn these parameters may be classified into:

- parameters related to the chemical nature of the filmogenous substance;
- parameters related to their ecological properties; viscosity, content of dry substance a.s.o.

Since the experiments have been performed with the use of polyurethane adhesives, the further references will be made in relation to this category of adhesives.

In the case of polyurethane adhesives, starting from a polyesther which contains a hidroxile group along the chain, a link of this group to a izocyanate occurs by a reaction of polyadition:



c) *Parameters related to the technology of adhesion.* Out of the technologic parameters which influence the resistance of adhesion one may remind: the time of pression and the value of the pression, the time of expectance from the deposit of the film on the sublayer up to a certain degree of adhesiveness by a partial elimination of the solvent from the filmogenous substance, the number of the layers obtained by repeated deposits of the adhesives, the activation of the film deposit (activation time and temperature).

2. Experiments. Technological Variants. The experiments were carried out by using some sublayers of DUROCOL rubber, ADEROM-551 (polyurethane adhesive) and DESMODUR (isocyanate).

The variable parameters that were taken into account are:

- the percentage of structure agent;
- the number of the layers achieved by deposits of adhesive;
- the activation time;
- the time of pressure of the sublayers.

To obtain some reproductible results, a series of parameters have been maintained constant:

- the same type of adhesive with characteristics according to the standards;
- the same type of rubber;
- the time for drying the film after deposits (20 min.);
- the same conditions of preparation of the sublayers.

Since the further processings will be performed using the method of the factorial experiment 2^n, the number of distinct dots and therefore, the number of experiments to be performed is given by the formula:

$$N = 2^n = 2^3 = 8.$$

In these conditions, the proposed technological variants were those given in Table 1.

Table 1

Number of experience	1	2	3	4	5	6	7	8
Activation time (s)	20	40	40	40	20	20	20	40
Number of layers	2	4	2	2	4	4	2	4
Pressure time (s)	10	10	30	10	30	10	30	30
Structure agent (%)	–	–	–	10	–	10	10	10

The technological variants were deducted after reading the matrix of the factorial experiment of the 2^3 type and was specified that the coded variables $U(i,j)$ have not the value +1; they correspond to the higher levels and the ones having the value –1 correspond to the lower levels (Table 2).

Table 2

Parameters levels	–	Activation time [s]	No. of layers	Pressure time [s]	Structure agent [%]	Resistance N/mm
Variation level	–	30	3	20	5	
Variation interval	–	10	1	10	5	
Lower lever	–	20	2	10	0	
Higher level	–	40	4	30	10	
j i	$U(0,j)$	$U(1,j)$	$U(2,j)$	$U(3,j)$	$U(4,j)$	$R(j)$
1	+1	–1	–1	–1	–1	3.30
2	+1	+1	+1	–1	–1	3.57
3	+1	+1	–1	+1	–1	4.15
4	+1	+1	–1	–1	+1	3.23
5	+1	–1	+1	+1	–1	5.09
6	+1	–1	+1	–1	+1	4.75
7	+1	–1	–1	+1	+1	3.93
8	+1	+1	+1	+1	+1	4.80

3. A Mathematic Model and a Programme for Data Processing. For the phenomenon under study the following mathematic model is proposed:

$$y = b_0 \cdot x_0 + b_1 \cdot x_1 + b_2 \cdot x_2 + b_3 \cdot x_3 + b_4 \cdot x_4,$$

were: b_0, b_1, b_2, b_3, b_4 are coefficients of regression; x_0, x_1, x_2, x_3, x_4 are variable parameters taken into consideration.

Table 3

Data	x_0	x_1	x_2	x_3	x_4
1. N_v	–	30	3	20	5
2. I_v	–	10	1	10	5
3. N_i	–	20	2	10	0
4. N_s	–	40	4	30	10
5. $b(i)$	4.19	–0.77	0.3625	0.3025	0.1625

As a consequence of the processing of the data by means of the programme in BASIC we have obtained the results given in Table 3.

In these conditions the obtained model has the shape:

$$y = 4.19 - 0.077x_1 + 0.3625x_2 + 0.3025x_3 + 0.1625x_4.$$

Further on, the continuation of the normal variables and to find the real mathematic model are suggested.

To obtain the normal variables it was used the following formula:

$$x = \frac{2X - (N_s + N_i)}{N_s - N_i},$$

where: x – the normal variables; X – the variable parameter; N_s – the higher level; N_i – the lower level.

In such conditions, in the mathematical model has been found out the necessary transformations are to be made and the mathematical model becomes:

$$y = 2.56 - 0.007X_1 + 0.36X_2 + 0.03X_3 + 0.032X_4$$

If the parameters X_1, X_2, X_3 are settled at the level of the lower limit, the equation becomes: $y = 3.5663 + 0.032X_4$.

4. Results and Disscusions. Out of a comparative analysis of the plots on the two curves (Fig. 2) one can draw the conclusion that the proposed mathematical model (curve *1*) does not reflect exactly enough the phenomenon under investigation, at least from the standpoint of the influence of the percentage of the structuring agent.

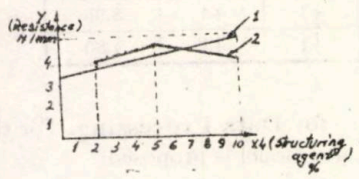


Fig. 2

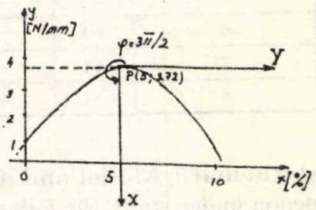


Fig. 3

The decrease of the resistance in the conditions in which the percentage of the structuring agent increase from 5% to 10% can be dued to the lack of adhesion

of the film to substrate. As the percentage of the structuring agent increases, the solution obtained in this way has an easier calibration (a fact that can be verified by following the calibration diameter), with consequences of the adhesion and finally on the resistance of the film.

One starts from the hypothesis that the resulted points after the experiments are located on a parable. Therefore the question of finding the equation of this parable appears, as it is known that the parable would degenerate in two straight lines which are concurrent (curve *2*). The equation of one of this lines is known from the previous steps: $y = 3.566 + 0.032X_4$.

Generally written, the equation of the line is: $n \cdot x - y + m = 0$.

Multiplicating two such equations it is obtained:

$$n_1 \cdot n_2 \cdot x - (n_1 + n_2)x \cdot y + y + (n_1 \cdot m_2 + n_2 \cdot m_1)x + (m_1 + m_2)y + m_1 \cdot m_2 = 0,$$

which represents the equation of a conic according to the theory of differential geometry.

In order that conic should represent a parable it is necessary that:

$$D = \begin{vmatrix} n_1 \cdot n_2 & -(n_1 + n_2)/2 \\ -(n_1 + n_2)/2 & -1 \end{vmatrix}.$$

In this case, the equation of the conic becomes:

$$-1.58x^2 + 49.5xy + y^2 - 168.68x - 255.03y + 896.74 = 0.$$

It arises the problem to find the canonic form of the parable under the form:

$$Y = 2pX,$$

where: $p = -D/(a_{11} + a_{22})^3$ and $D = \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix}$ and $a_{11} = -1.58$; $a_{12} = a_{21} = 24.75$; $a_{22} = 1$; $a_{13} = a_{31} = -84.32$; $a_{23} = a_{32} = -127.5$; $a_{33} = 869.74$.

In these conditions, $D = 13.39$ and $p = 8.28$. The axis OX of the parable is $X = 5$, the axis OX is rotated to the axis OX with $\varphi = 3\pi/2$. The axis OY is tangent at the peak of the parable in $P(5, 3.72)$ (Fig. 3).

With these data one can plot the parable that reflects better the phenomenon investigated (the influence of the percentage agent of structure when $x_1 = 20$ s, $x_2 = 2$ s and $x_3 = 10$ s).

5. Conclusions. This discussion was for only one case, obtaining thus only one curve. If in the mathematical model found here the variables x_1, x_2, x_3 are replaced with other values situated within the corresponding variation interval, each time it will be obtained an other equation under the form $Y = pX$ and, following the algorithm presented in this chapter, one can determine some other values for the coefficient p from the conic equation of the parable.

Thus, a family of parables is obtained, each one reflecting the phenomenon investigated in certain conditions.

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CONTRIBUŢII LA MODELAREA MATEMATICĂ A PROCESELOR DE LIPIRE ÎN INDUSTRIA DE ÎNCĂLŢĂMINTE

(Rezumat)

Se prezintă o serie de aspecte legate de lipirea cu adezivi poliuretanici, specifice industriei de încălţăminte, precum şi rezultatele obţinute în urma efectuării unor experienţe în condiţii date. Datele au fost prelucrate cu ajutorul unui program în limbaj BASIC. Lucrarea îşi găseşte aplicaţie în condiţiile în care se doreşte o optimizare a proceselor de lipire, în ansamblul general al procesului de confecţionare a încălţămintei.

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Secţia VIII
TEXTILE. PIELĂRIE

RESTRUCTURING ROMANIAN INDUSTRY BY RESTRUCTURING THE MIND-SET OF THE INDIVIDUALS WITHIN ITS ORGANIZATIONS

BY
MARK CHALLINOR and KEVIN JOHNSTON

1. Current Western HRM Theory – Questions of Ownership. It is appropriate at this juncture to consider the question of ownership and control of organisations. This is a central issue in "Maximizing shareholders wealth" is a frequently quoted maxim applied to such questions as "whose interests should business organisations serve?". Although there are many examples of organisations which exist to benefit a variety of stakeholders and interest groups, the majority are nominally aimed at making profits for the owners. If wealth maximization, therefore, is taken as the corporate *raison d'etre*, it does not seem surprising that operational management should be perceived as being essentially "actuators" from whom no recognition of parochial needs is expected. It could be argued that management who allow their organisation to lose profit opportunities by accommodating staff requirements are failing in their duty to the shareholders. For the purposes of this paper, however, pragmatism and opportunism are taken to indicate a short-term and "knee-jerk" mentality in management.

The issue of Human Resource Management (HRM) is compounded by the plethora of material relating to techniques such as job enrichment. These techniques, *inter alia*, seek the amelioration of staff/management dissonance and consequent organisational disfunction by allowing the workplace to become a cradle of self-development and self actualisation. It should not be forgotten, however, that shareholder wealth is maximized by a more productive workforce. HRM research has largely centred on improving effectiveness and this is seen by some as reinforcing the notion that even those firms who attempt to allow interest groups (particularly staff) to further their own interests in the working environment, ultimately do so to improve "bottom-line" results. This further suggests that even companies perceived as being "paternal", have the wealth maximization ethic as their primary and over-riding agenda even if this remains hidden.

2. Human Resource Management – the Debate. Central to the debate is the question: what is Human Resource Management? a question of perspective. Different interest groups appear to differ in their definitions, this may of course

simply reflect a degree of parochial self-interest. There are, however, differences within the interest groups themselves. A simple example of this comflict is seen in the differing viewpoints of devotees of the Pluralist and Unitarist schools of management as defined by F o x (1983).

Pluralist managers are said to accept that organisations are merely a "portmanteau" concept which encompasses the totality of the objectives and behaviour of those humans within them. It follows that Pluralists seek to mitigate the needs of differing interest groups within the organisation and that their actions reflect this in a degree of "satisficing". (It could also be said that this group are philosophically existentialist). Proponents of the Unitary approach appear ultimately to endow the organisation with a life of its own. The organisation thus effectively exercises a benign autocracy which seeks to reward employees for following managerial imperatives without debate. The dividing factor between the schools appears to be that Unitarists cite the organisations interest as the prime concern; satisficing is, therefore, not a conscious issue.

Definitions of HRM vary accordingly. S i s s o n in 1986 asserts : "HRM is resource centred not workforce centred, *id est*, fulfills management needs."

This is likely to be a definition acceptable to Unitarists.

S p a t e s (1988), on the other hand, adopts a pluralist orientation in describing HRM as: "Organising individuals at work so that they will get the greatest possible realisation of their intrinsec abilities."

It is open to speculation whether this realisation is desirable purely for the individual or as a mechanism whereby the organisation derives greater benefit from its employees.

S t o r e y (1990) identifies a "hard" and "soft" version of HRM. The former seeks the maximisation of economic returns of the labour resource, the latter seeks the release of the "untapped reserves of human resourcefulness" by an increase in employee paricipation, commitment and involvement.

S t o r e y also suggests that there is evidence to suggest that HRM represents the "Balkanisation" of personnel predicted by T y s o n (1986).

A con-comitant of the debate is the need to distinguish between Personnel Management and HRM. According to some, HRM is characterised by the subordination of an individual's needs to those of the organisation. It is not inappropriate to draw parallels here with the theories of the Scientific school of management as characterised by T a y l o r et al. (1961). Paralles could also be drawn here with McG r e g o r's theory X (1987). In this school of thought, individuals become a homogeneous group and the traditional Personnel approach of collective mediation is applied. This view has much in common with the unitary approach. Others take the view that HRM is distinct from personnel management because it seeks the integration of people management into the line management function. Personnel management has also been defined as being merely tactical or pragmatic, concerning itself in reactive way to managing the relationship between management and workforce.

An alternative viewpoint defines and differentiates HRM from Personnel man-

agement by introducing the "strategic element". It is believed by some that HRM simply relates to the exercise of the personnel function at a higher level, decisions regarding the allocation of resources rather than just skills become the focus. The implication here is that it is the scope of the function which characterises the divide between HRM and the personnel function.

To continue to list definitions would be purely iterative and serve no purpose. The variety of opinions is, however, indicative of the dilemma that faces an organisation which wishes to embrace HRM.

These varied definitions of HRM are not neccessarily mutually exclusive, and share a common theme in that they evince a continuing and developing obligation on organisations to recognise the contribution of personnel specialists to an organisation. With employee skills becoming an ever more critical determinant of company's success, the personnel specialist can no longer be seen (as D r u c k e r in 1986 would have it) as the "dustbin" of unwanted line management tasks.

Furthermore, since strategic planning has become the primary management tool of the last twenty years, it seems appropriate that the notion of managing human resources in a strategic manner has also gained credence and authority.

It may be seen that attempting a global definition of HRM in terms of style or system is specious. It is more appropriate perhaps, to define HRM as the use of whatever tools and models are appropriate to get the best out of the human resource.

For the purposes of this analysis, however, the following is offered as a working definition of HRM:

"The term Human Resource Management is not just a new whim but signifies a total approach to the problems of managing people in organisations. It is an integrated approach which involves not only the specialists in an advisory role but also the managers generally." (L y n a s, 1986)

3. Romania – Current Practices in HRM. Recent changes in economic climate might be said to require Romania to employ a different kind of staff, people who are used to taking responsability for themselves and who would be comfortable with the devolution of operational issues from higher authority.

It follows from the above that to achieve effective strategic HRM, Romania would need to consider changes in areas such as appraisal, reward, training, job design and staff development. A re-evaluation of the type of staff to be recruited, together with a review of corporate "culture" and structure would also seem appropriate.

Perhaps the most important indicator of a company's attitude to HRM is its recruitment policy. In general, Romanian industry espouses the notion of a non-discriminatory ethos. Where they exist, however, Romanian Personnel managers appear to be involved only at a functional level. The debasing of the personnel function in this regard may be viewed as a strong indicator that Romanian industry has neither a cogent strategy nor any great regard for the true notion of HRM. This has obvious implications for job satisfaction and motivation since the wrong staff may be recruited for the wrong reasons.

There are currently few formal job descriptions extant in Romanian firms. Management need to rectify this point and at the same time set up mechanisms appropriate for the review of descriptions. Additionally, the personnel function should have responsability for both this and continuing recruitment in partnership *with the appropriate line-management.*

The link between effective processes of leadership and motivation and employee relations is cited by T h o m a s o n as a critical HRM concern. Aside from the matters of job design, reward, etc, the corporate culture has a large part to play here. Training in Romania is minimal; management development in terms of education is also embryonic by Western standards (but growing). A coherent strategy of management education and development is clearly required if the inculcation of social norms as guides for conduct and cultural reinforcement are to be achieved throughout industry. This need should not be left to Government and educators and is indeed more correctly initiated by management in industry.

Appraisal (where it exists in Romania) appears to centre around issues of productivity and sales. Many employees may view the appraisal system as a mechanism of control, with poor peformance castigated and outstanding performance (as currently perceived) rewarded. Certainly current practice is mechanistic and aimed at control, the fundamental principle of appraisal (centrality of participation) has not yet been recognised by the majority of Romanian management. It would seem that an obvious need exists to change the current system to allow participants some greater proactivity via self-development. Clearly the appraisal system needs to be closely allied to training.

Reward mechanisms in Romania appear to be linked to the output or in many cases is determined by a statistical mechanism linked to the number of days worked. It follows that pay is determined by inappropriate factors. It would similarly be a mistake to allow volume rather than quality to become the key to enhanced remuneration. The definition of new job descriptions shoud lead to new reward criteria. Intrinsec rewards also need to be considered for the long term.

T h o m a s o n (1984) asserts that the *"de-emphasis of an exploitive individualism"* is central to any acceptable perspective on maintaining effective employee relations. If this view is accepted as appropriate to Romania in its present form, then cultural changes would appear to be another determinant of an effective future HRM policy. The current marginalisation of some staff owes much to the lack of emphasis on the individual and his/her self-development.

4. Questions of Structure and Organisational Development. Our previous discussion explored current HRM practice in Romania and attempted to offer solutions to some of the problems identified. F o u c a u l t (1976) amongst others, however, would claim that to try to change practices within organisational subsystems without re-appraising organisational structure is simply "bricollage". M o r g a n and B u r r e l l (1979) offer a model to measure and assess the congruence (or otherwise) between subsystems. This seeks to "fit" a straight line to a profile matrix, organisation whose practices show a non linear progression are labelled "incongruent". In this context Romania could still be perceived to be in-

congruent, even in light of the changes proposed in the previous section, since a mechanistic structure persists in a period of turbulence and instability.

The labels of pragmatism and opportunism can validly be attached to the operational management of Romania. Despite the apparent recognition of the value of the human resource shown by many companies which we visited, the subsequent actions of operational management tended to believe this. Clearly a more fundamental change is required, structure and culture are the key issues in this regard.

It is reasonable to say that the current management modus operandi in Romania seeks at best to suggest a change in cultural artifacts, the deep assumptions and beliefs of the management appear to remain dominated by issues of power and control inappropriate to the new operational environment. M o r g a n (1980) has identified what he terms "egocentric" organisations. The fundamental feature of these firms is their overriding concern to promote their own self-interest and perceived identity against the outside world. This is manifested by organisations continuing to produce outdated goods or sevices and/or by an inability or unwillingness to change culture or structure to meet a changing environment.

The question of culture comes into play strongly at this point in the analysis. Change as a driver of cultural adaption has been strongly advocated by S c h e i n. there is, however, a central dilemma to this. If the prevailing management culture is to cling to the old ways then how can true change be effected? Certainly if a new structure is to be put into place, the ability of senior management to adopt and encourage the change must be in doubt in the case of Romania.

We have suggested that current management policy at Romania is still heavily weighted around traditional themes of a specialist mechanistic workforce. The Taylorist principle of gathering knowledge from the workforce and giving this to the management still dominates. The maintainence of narrow specialism is a particularly strong indicator of management's lack of true understanding of strategic HRM imperatives.

In the light of these assertions, it seems appropriate to suggest an alternative approach for Romanian industry which responds in a truly strategic manner to recent changes. It is also necessary to consider the tools required from a human resource perspective to manage this transition effectively. What is required is reflected in the adaptation of the theory of autopoiesis described by M o r g a n (*op.cit.*) as: "(an ability) to explore possible identities and the conditions under which they can be realised."

M o r g a n goes on to suggest that an autopoietic organisation evolve its identity along with the wider systemic environment, rather than in spite of it.

5. New Structures. Given the nature of the World and European Economic situation and its impact on both Romania and its extant and potential international markets, a model for an integrated and multi-skilled workforce needs to be found or developed. Suggested key characteristics and advantages of the new organisations should be:

– devolution of operational responsability from senior level to self-managed

operational teams;

- interaction between specialists and knowledge pooling;
- enhaced socio-organisational aspects; motivation, personal development, technical training;
- a tacit psychological contact between workers and management;
- a responsive and adaptive approach to volatile environments;
- a competitive advantage over non-adaptive competition;
- the provision of value added services via a personal approach;
- flexible and (if appropriate) internationalist;
- resource supported by former line management function;
- flatter and "matrixed" not hierarchical;
- recursive;
- aware of the need for continuous and discontinuous change;
- tolerant of mistakes, viewed as learning opportunities.

An adapted "Matrix" structure similar to that proposed by M i n t z b e r g (1985) appears to be appropriate. This seeks to allow a formally recognised lateral dimension which facilitates multi directional authority, influence and control. Using this model staff could liase with senior management to allow the implementation of new imperatives. The particular attraction of this model stems from its base in traditional hierarchical structures, this may make an acceptance of change easier from the point of view of management and workforce alike.

The proposed new structure has added attractions from Romania's point of view. The integration of functions within firms leads to a more generalist workforce, emphasis shifts from competition to collaboration since the polarisation of specialism is broken down. M o r g a n's notion of a boundary spanning unit can become a reality in a matrix organisation. Individual branch units can use their direct access to the environment to alter and shape their approach to decision making. The intelligence gathered by such units can be used both laterally and vertically but represents a change from the traditional "tablets of stone" mentality evident in most hierarchies. The definition of appropriate tools for cultural change is a more difficult matter. Certainly issues such as obtaining the power to effect the change is of significance as is the notion of gaining a "critical mass" of support. Organisational Behaviour (OB) literature abounds with theories of change management which are both diverse and sometimes opposed and for that reason it is not considered appropriate to attempt prescriptions in this paper.

Y o u n g (1987), however, adopts a generalist approach which may be of some use to the management of Romania. Y o u n g cites the following as components of a good manager of change:

- Extensive macro and micro environmental understanding;
- Cognition of appropriate approach to change in a given organisation;
- Temperamental suitability to particular change needs;
- Ability to direct, and understanding of, the "levers" of change;
- A clear and subtle understanding of the complexities of the organisation to be changed so that *appropriate* change is fostered;

– Devolution of operational responsability from senior level to self-managed operational teams;

– Interaction between specialists and knowledge pooling;

– Enhanced socio-organisational aspects: motivation, personal development. technical training.

Y o u n g goes on to say: "In short, the balanced capacity to read the environment, understand the change implications, know what this means for their organisation and manage change appropriately is one of the most important management skills for the 1990s and beyond."

Certainly a critical factor in any true application of HRM in Romania would be the appointment of an HRM director to the main board of directors of firms. A champion of change who posseses a wide portfolio of OB, HRM and Organisational Development (OD) techniques is necessary to counter the likely intransigence of operational management. The notion of moving from "contract to trust" is certainly far removed from the current state of Romania (and indeed many companies in Western Europe!) and we do not suggest that changes will be easy or necessarilly welcome in many quarters!

6. Some General Conclusions. This paper was based around a thesis, the central premise of which was that Romanian management, despite espousing ever more sophisticated management skills, remain short term and tactical failing to address HRM definitions and distinctions which the authors have shared with you have a common theme in that they all appear to advocate a more eclectic and strategic approach. It may however come to pass that HRM is seen in Romania as just another "fad". The key to the successful inception of HRM may well lie in not attempting a prescriptive and palliative definition, but rather in embracing a new ethos of management which accepts that organisations exist in chaotic environments and that constant organic change and repositioning is necessary. A learning, recursive organisation may well be one way toward achieving this. Other concepts such as the notion of "building in slack" to organisations to allow a reflective influence, would seek to avoid the mechanistic application of a "bible" of HRM practice. It may be that the only truly worthwhile "culture" is one which constantly changes in response to its environment – a view shared by D r u c k e r (1993).

A more fundamental problem with HRM as a new way forward may lie in the language which describes it. Both F o u c a u l t (*op.cit.*) and B a r t h e s (1978) argue for the use of "Paralanguage", this area of study derives from the central dilemma that organisations face in interacting with and describing their environment. It is contended that people work within the "cracks" of the official and formal fabric of organisations. The rationale for this derives from the assertion that the official language and symbolism of an organisation may be inappropriate in that it is not able to adequately describe the true environment and cultural artifacts which actually exist within the firm. Following logically from this is the idea that to plan change or development in organisations using today's language and concepts may simply perpetuate this lack of congruence between what *is actually done* in

order to operate efficiently and what is officially *said to be done*. What is need (it may be argued) is the development of language and symbols which better reflect the environment. Obviously the development of this new language cannot take place in an interregnum, and so it is necessary to mix and adapt the old with the newly emerging. The need for Paralanguage can be laterally illustrated by considering the tendency of organisations to rewrite history in order to justify future plans. This propensity for "historicity" may have links with the egocentricity previously discussed.

Whilst many Romanian managers might recognise the intellectual validity of Paralanguage, they may well view it as a truism destined to remain the "property" of theorists and academics. If this is the case it could be argued that the practice of HRM will remain "pragmatic and opportunistic" and as a paradigm it will loose favour as so many potentially valuable theories have before.

If, however, the view is taken that the use of paralanguage might be considered logical and of practical value in increasing an organisation's competitive advantage then there can be few organisations in Romania or indeed in the West who can say that they are exploring the full potential of Human Resource Management. Romania appears to be low in the evolutionary scale in this regard. The first step in climbing the "mountains of change" rests with you as individual academics and managers. You must become champions of change using your power and influence to initiate and sustain change. You must also help all memebers of your organisation to understand the need for change give them ownership and the power to effect change.

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RESTRUCTURAREA INDUSTRIEI ROMÂNEŞTI PRIN REORIENTAREA GÂNDIRII MEMBRILOR ORGANIZAŢIILOR SALE

(Rezumat)

Industria românească are nevoie de o schimbare radicală a modului de abordare a Managementului Resurselor Umane. Este necesară o revizuire a structurilor şi practicii de personal. Folosirea unui nou limbaj de imitare a practicilor occidentale nu schimbă politica internă în sine.

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ON THE DISJUNCTIVE LOGIC PROGRAMMING

BY
VALERIA SLABU

1. Introduction. The first theoretical developments in the disjunctive logic programming were by Jack Minker and two of his students Arcot Rajasekar and Jorge Lobo. This presented in [1] the historian of the foundation of disjunctive logic programming.

Upon the theoretical treatment of Horn logic programming developed of K.R. A p t, M.H. Emden, K.L. Clarck, R.A. Kowalski, J.W. Lloyd, J.L. Lassez and M.J. Maher built and detail declarative and operational semantics of the disjunctive logic programs besides the three mentioned above and K.R. Apt, H.A. Blair, A. Walker, M. Gelfond, V. Lifschitz, T. Przymussinski and H. Przymussinski.

Of course the two panel of research workers can be continued here enumerating just those researchers who initiated and solved the theoretical foundation of Horn logic programming and disjunctive logic programming.

Beginning with 1980, J. Minker and his two students published the few articles [2] and [3] in which the main results of disjunctive logic programming were present and prove, such as: the fixpoint semantics for the positive and general disjunctive logic programs, the procedural definition of negation, the equivalence of the proof procedure method and the minimal models approach with the procedural and the declarative semantics for negation.

At the Logic Programming Conference in 1980, Topor stated the terminology of disjunctive database and disjunctive logic programs.

Many questions of disjunctive logic programming such as, to compute answers to queries in general disjunctive programs, the relationship between several forms of nonmonotonic reasoning (circumscription, autoepistemic and default reasoning) and disjunctive logic semantics are still opened and now.

2. Disjunctive Logic Programs

2.1. Basic Definitions. First of all we discuss the usual notions of term, atom, literal and well-formed first order formula.

A first order theory we mean an alphabet a first order language, a set of axioms and a collection of inference rules. Any alphabet A of a first order language L is assumed to contain: a) a countably infinite set of variable symbols; b) a set

of constant, function and predicative symbols; c) connectives ($\wedge$, $\vee$, $-$, $\rightarrow$) and quantifiers ($\exists$, $\forall$); d) usual punctuation symbols (, ( )). The arities of functions are > 0, the arities of predicates are ≥ 0 and functions of arities $= 0$ are constants.

The first order language L over the alphabet A is defined as the set of all well-formed first order formulae that can built starting from the atoms and using connectives, quantifiers and punctuation symbols in a standard way.

The terms and the well – formed first order formula are defined inductively.

A term is defined as follows:

a) a variable is called the term;

b) a constant is called the term;

c) if f is a n-ary function symbol and $t_1, ..., t_n$ are terms, then $f(t_1, t_2, ..., t_n)$ is a term.

Let $t_1, ..., t_n$ be the terms and let p be a n-ary symbol predicative, $p(t_1, t_2, ..., t_n)$ is called an atomic formula or, in short an atom.

A well-formed first order formula or, more simply, formula is defined as follows:

a) an atom is called the formula;

b) if F is a formula then $(\sim F)$ is a formula;

c) if F and G are formulas then $(F * G)$ is a formula, and $* \in \{\vee, \wedge, \rightarrow, \leftrightarrow\}$;

d) if F is a formula and x is a variable, then $(\forall\, x\ F)$ and $(\exists\, x\ F)$ are formulas.

The scope of $\forall x$(resp. $\exists x$) in $\forall x F$(resp. $\exists x F$) is F.

A bound occurence of a variable in a formula is an occurence immediately following a quantifier or are occurence within the scope a quantifier, which has the same variable immediately after the quantifier. Any other occurence of a variable is free. A closed formula is a formula with no free occurence of any variable.

If F is a formula and $y_1, y_2, ..., y_n$ are the all variables which have a free occurence in F, then $(\forall y_1 \forall y_2 ... \forall y_n)F$ denotes the universal closure of F or, more simply, $\forall(F)$. Similary, $\exists(F)$ denotes the existential closure of F.

2.2. Clauses and Programs. The main class of formulas discussed here are clauses.

They are occuring in the Horn logic programs and in the disjunctive logic programes.

Definition 1.2.1. A clause is a formula of the forme $\forall y_1 ... \forall y_r (L_1 \vee ... \vee L_m)$, where each L_i is a literal, with $i = \overline{1, m}$ and y_j, with $j = \overline{1, k}$, are variables occuring in L_i.

We will assume for any clause that the negative atoms occur to after the positive atoms. As conjunction is commutative, there is no loss of generality in making this assumption.

Throughout, we will denote the clause:

$$\forall y_1 ... \forall y_k\ (A_1 \vee ... \vee A_n\ \vee \sim B_1 \vee ... \vee \sim B_r),\ n \geq 1,\ \ r \geq 0,$$

where $A_1, ..., A_k, B_1, ..., B_r$ are atoms and $y_1, ..., y_k$ are all the variables occuring in these, by $A_1, ... A_n \leftarrow B_1, ..., B_r$. We do not differentiate between the two forms in which clausses are represented but rather wiew the former as a precise way of representing the latter.

In the conclusion, a clause is a construction of the form headbody, where the head is a disjunction of literals and the body is either the logic value true or, a finite conjunction of literals. Consequenty, the commas in the antecedent $B_1, ..., B_r$ denote conjunction and the commas in the consequent $A_1, ..., A_n$ denote disjunction. If $n = 1$ then the clause is called a Horn Clause or a program clause. If $n \geq 2$ then the clause is called indefini clause or disjunctive clause.

A clause of the form $A_1, ..., A_n \leftarrow (\overline{y}_1 B_1)...(\overline{y}_r B_r)$, where B_i, with $i = \overline{1, r}$, are literals and $\overline{y}_i$ is a subset of the variables, possible empty, occuring in B_i is called a first order disjunctive clause.

A unit clause is a expression of the form $A \leftarrow$, that is a program clause that has no body. An assertion clause is a clause that has no body.

A goal clause or a query is an expression of the form $\leftarrow$ body. We also can use the following alternative notation for goal clauses such:

a) $\leftarrow B_1, ..., B_m$, $m \geq 0$, where the term $B_1, ..., B_m$ is a conjunction of atoms;

b) $\sim \exists y_1, ..., \exists y_s \ (B_1 \wedge ... \wedge B_m)$;

c) $\forall y_1 ... \forall y_s \ (\sim B_1 \vee .. \vee \sim B_m)$.

A query is definite if it is a single conjunction of literals, otherwise it is indefinite. The empty clause, denoted $\square$, is the clause with empty consequent and empty antecedent. This clause is to be understood as a contradiction.

Definition 1.2.2. A logic program or Horn program is a finite set of program clauses. A disjunctive program is a finite set of disjunctive clauses. Disjunctive logic programs are natural extensions of Horn logic programs used to represent indefinite information.

The informal semantics of the disjunctive clause is for each assignment of each variable, if $B_1, ..., B_r$ are all true, then there is i, with $i = \overline{1, n}$, so that A_i is true. An assertion clause is unconditional. Its informal semantics is for each assignment of each variable, there is i with $\overline{1, n}$, so that A_i is true. A predicative symbole r is disjunctive in the disjunctive logic program if r occurs in any head of the disjunctive clause. In a disjunctive logic program the set of all program clauses with the same predicate p in the head is called the definition of p. If p and q are two predicative symbols in the disjunctive program P, then q will refere p if there is a clause in P with q in her head and p or in the head, or in her body. Other details and examples are in [4].

Each ensemble program-goal needs return an answer different of yes/non. An answer of a query G over program P is either logic value False or, a disjunction of instances of conjunction in G over the alphabet of P and Q, that is a disjunction of conjunctions obtained from those in Q by substituing variables by terms of the alphabet used to write P and Q. An answer is definite if it consists of a single conjunctions otherwise it is indefinite. An answer False is the most general answer to any query over an inconsistent program. A definite query may have just indefinite answer. An indefinite may have both indefinite and definite answers.

3. Models of the Disjunctive Logic Program. Van Emden, Kowalski and Apt defined the fixpoint declarative semantics (denoted and denotational) based on the models theory and the procedural semantics (denoted and operational) based on the

proof theory for the Horn logic programs (many details in [4]). These semantics are utilised, in particular, for to establish the soudness and the completeness of SLD-resolution (beside the success and fail set) of the PROLOG interpreter. Standard PROLOG systems employ the computation rule which always selects the leftmost atom in a goal together with a depth-first search rule in the SLD-tree. In the proof the equivalence of the fixpoint semantics with the procedural semantics has been used the fixpoint techniques. Lorge Lobo, Jack Minker and Arcot Rajasekar extend in [3] the fixpoint semantics and the procedural semantics for the disjunctive logic program and proved their equivalence.

3.1. Herbrand Interpretations. For the demonstrate the truth of falsity of formulas it is necessary to attach some meaning to each of the symbols in the formula. The quantifiers and connectives have a fixed meaning, but meaning the attached to the constants, functions and predicatives symbols can vary.

An interpretation simply consists of some domain over which the variables range, the assignment of each constant to an element of the domain, the assignment of each function to a mapping on the domain and the assignment of each predicate to a relation on the domain. The interpretation which gives the principal meaning of the symbols is called the intended interpretation. The class of Herbrand interpretations is a much smaller and more convenient class of the interpretations in the study of logic programming systems.

Definition 3.1.1. A ground term is a term not containg variables.

A ground atom is an atom not containg variables.

Definition 3.1.2. Let L be a first order langauge. The Herbrand Universe U_L for L is the set of all ground terms, which can be formed out of the constants and functions appearing in L. In the case that L has no constants, we add some constant to form ground terms. The Herbrand base B_L for L is the set of all ground atoms which can be formed by using predicates from L with ground terms from the Herbrand universe as arguments. The extended Herbrand base EB_L for L is the set of all positive clauses which can be formed using distinct ground atoms from B_L. The extended Herbrand base of size-k positive clause EB_P^k of program P is the set of all positive clauses formed by taking the disjunction of k distinct ground atoms from the Herbrand base of the program P.

If $EB_k(P)$ denoted $\bigcup_{i=1}^{k} EB_P^i$ then the extended Herbrand base of P can defined as follows: $EB_P = EB_\infty(P) = \bigcup_{i=1}^{\infty} EB_P^i$.

Obvious, EB_P^1 is the Herbrand base of the program P, that is $EB_P^1 = EB_1(P) = B_P$.

Definition 3.1.3. Let L be a first order language. An interpretation for L is a Herbrand interpretation if the following conditions are satisfied:

a) the domain of interpretation is the Herbrand universe U_L;

b) constants in L are assigned to them selves in U_L;

c) if f is an n-ary function in L, then f is assigned to the mapping from $(U_L)^n$ into U_L defined by $(t_1, ..., t_n) \to f(t_1, ..., t_n)$, where t_i, with $i = \overline{1,n}$, is the term.

On the assignments of the predicates in L are no restriction, on that different Herbrand interpretation arise by taking different such assignments. Thus, it is

possible to identify a Herbrand interpretation with a subset of the Herbrand base of L. The Herbrand interpretation is the set of all ground atoms which are true w.r.t. the interpretation. Conversely, given an arbitrary subset of the Herbrand base, there is a corresponding Herbrand interpretation defined by specifying that predicates map to "true" precisely when the predicate applied to it is arguments is in the given subset. Thus, this remark can be taken the definition of the Herbrand interpretation. In the literature beside this definition there are the two more definition, as follow:

- Let L be a first order language and B be the set of all closed atomic formulas over L. Let $B' = (B_0, B_1, ...)$ be a linear order of set B which can be a finite set or a countable infinite set. A Herbrand interpretation h identified with a range of elements, $h = (e_0B_0, e_1B_1, ...)$ such that for any $B_j = e_jp(t_1, ..., t_n)$, $ej = \wedge$ (the empty side) if the atoms $p(t_1, t_2, ..., t_n)$ is true w.r.t. the interpretation h and $ej = \sim$ if the atoms $p(t_1, ..., t_n)$ is false w.r.t. the interpretation h, where t_i is terms, with $i = \overline{1,n}$.

- Consider L and B' about the second definition. Then a Herbrand interpretation can be representing as a semantic tree. There is a mapping one-one between a Herbrand interpretation set and a branch set of the semantic tree.

Example 3.1.3. Let $L = (p, q, r)$. There are eight Herbrand interpretations. For instance, consider h the follow Herbrand interpretation $\{p, r\}$.

- Then p and r are true w.r.t. h, but q is false w.r.t. h.
- The Herbrand interpretation can give as follow $(p, \sim q, r)$.
- The semantic tree of all Herbrand interpretations is eight branches.

3.2. Answer Substitutions. Answer substitutions is a crucial concept of the logic programming and the many researchs are undertaking for it study. This concept is, in fact, the declarative understanding of the output from a program and a goal. First of all we introduce a new form the substitution which will be using in the next paper where we discuss the procedural semantics of the disjunctive logic programs.

Definition 3.2.1. A substitution θ is a any countably infinite set of terms, $\theta = (t_0, t_1, ...)$.

For the some substitutions will be the easy notation $(V_{j_1}/s_1, V_{j_2}/s_2, ..., V_{j_n}/s_n)$, where $V_{j_1}, ..., V_{j_n}$ are the distinct variables. In the such situations will understand the substitution in that $t_{j_k} = s_k$ for $k = 1, 2, ..., n$ and $t_j = V_j$ if $j \neq j_1, j_2, ..., j_n$.

Example 3.2.1. $(V_1/s_1, V_3/s_2, V_5/s_3) = (V_0, s_1, V_2, s_2, V_4, s_3, V_6, V_7, ...)$.

The substitution $\varepsilon = (V_0, V_1, ...)$ is called the identity substitution. In the first notation, the identity substitution is the empty set, that is $\varepsilon = (\ )$.

An expression E is either a term, a literal or a conjunction or disjunction of literals. Then $E\theta$, the instance of E by θ, is the expression obtained from E by simultaneous replacing each occurence of the variable V_i in E by the term $t_i, i = 0, 1, ...$

The elementary proprieties of substitutions are as follow:

a) $\theta\varepsilon = \varepsilon\theta = \theta$, for all substitution θ.

b) $(E\theta)\gamma = E(\theta\gamma)$, for all expression E but θ and γ are the substitutions.

c) $(\theta\gamma)\delta = \theta(\gamma\delta)$, for all substitutions θ, γ and δ. The proof is in [5].

Definition 3.2.2. Let P be a program and G be a goal. An answer substitution for $P \cup \{G\}$ is a substitution for variables of G.

An answer substitution does not necessary contain a bilding for every variable in G. If G has no variable then the answer substitution is the identity substitution.

Definition 3.2.3. Let P be a program and G be a goal $\leftarrow A_1, ..., A_k$. An answer substitution θ for $P \cup \{G\}$ is a correct answer substitution for $P \cup \{G\}$ if $\forall(A_1 \wedge ... \wedge A_k)\theta$ is a logical consequence for P. θ is a correct answer substitution for $P \cup \{G\}$ if $P \cup \{\sim ((A_1 \wedge ... \wedge A_k)\theta)$ is insatisfiable.

A correct answer substitution provides a declarative understanding of the desired output from a program and goal.

3.3. Least Stated Models. In contrast with the Horn logic programs, a disjunctive logic program can have many minimal models. For example, the program $P = \{p(a) \vee p(b)\}$ have two minimal models $\{p(a)\}$ and $\{p(b)\}$ and in addition, the program P rewrites either as in $P_1 = \{p(a) \leftarrow\sim p(b)\}$ or as in $P_2 = \{p(b) \leftarrow\sim p(a)\}$ and about the application of the fixpoint operator in the each distinct instance we obtain $T_{P_1} \uparrow \omega = \{p(a)\}$ or $T_{P_2} \uparrow \omega = \{p(b)\}$.

It is obvious that $p(a) \vee p(b)$ is a logical consequence of P, but neither $\{p(a)\}$ nor $\{p(b)\}$ is a logical consequence of P and thus the concept of the model minimal no capture the intended meaning. Instead there is a set of minimal Herbrand models that characterizes a disjunctive logic program.

Remark 3.3.1. A positive clause C is a logical consequence of a program P if C is true in every minimal model of P. That is, $P \vdash C$ if $\forall M \in MM(P)$, $M \models C$, where $MM(P)$ is denoted the set of minimal models of P.

Such, the declarative semantics defined for the Horn programs fails when a program is a disjunctive logic program. The stated model contain the set of based positive clauses which are the logical consequences of disjunctive logic program. The intended meaning of the disjunctive logic program will be characterizing of minimal stated model and there is as in the Horn logic program a closed relation between this and the fixpoint semantics. The minimal stated model is unique for the disjunctive logic program and every clause which is the logical consequence of P there is a clause of stated model which subsumed the clause.

Definition 3.3.1. Let P be a disjunctive logic program. A subset of the extended Herbrand base of P is called the state of P.

Definition 3.3.2. Let P be a disjunctive logic program. The stated model of P is a state S of P which carry out two conditions: every minimal model of P is a model of S and every model of S is a model of P.

A stated model M of P is minimal if no there is a stated model of P which is subset of M.

Every disjunctive logic program have a unique minimal stated model (MS_P) and every clause which is the logical consequence of disjunctive logic program there is a clause of MS_P which subsumed the clause.

The functions or relations computed by program are usually characterized mathematically by associating a certain mapping with each program. What is computed can then be regarded as a fixpoint of that mapping. In logic program-

ming such mappings and their fixpoints play a predominant role in the semantical characterizations. The fixpoints are subject to an order, so that we can distinguish the greatest and the least fixpoint as being of particular interest.

The least fixpoint is a limit of all finite powers of the mapping and it characterizes the positive information contained in a logic program. The greatest fixpoint bears some relationship to negative information contained in the program.

3.4. Fixpoint Semantics. For Horn programs, Van Emedn and Kowalski have shown that the fixpoint operator T_P is monotonic and hence has a least fixpoint. The continuity of T_P for P a Horn program is fundamental to the proof of many important results for this class of programs. The least fixpoint defines the intended meaning of a Horn program in the sense that the least fixpoint of the program is a Herbrand interpretation I such that an atom is in I if and only if it is a logical consequence of the program. In our instance, the fixpoint operator (the immediate consequence function) is applied on a complete lattice 2^{EB_P} which is formed using sets of all states of a disjunctive logic program.

2^{EB_P} is a complete lattice under the partial order of set inclusion $\subseteq$. The bottom element of the lattice is the null set, ϕ, and the top element is EB_P.

The closure operator that maps states to states of a disjunctive program P is defined as follow: $T_P : 2^{EB_P} \to 2^{EB_P}$, where $T_P(S) = \{C \in EB_P : C' \leftarrow B_1, ..., B_n$ is a ground instance of a clause in P, $\{B_1 \vee C_1, ..., B_n \vee C_n\} \subseteq S$, C_i can be null, $i = \overline{1,n}$, $C'' = C' \vee C_1 \vee ... \vee C_n$ and C is the smallest factor of $C''\}$, where S is a state of a program P (i.e., S is a subset of EB_P). The smallest factor of a ground clause C' is defined as the clause C such that C contains only distinct atoms and $C \Longleftrightarrow C'$.

For the positive disjunctive program the fixpoint operator T_P is continuous hence monotonic and achieves a least fixpoint. The least fixpoint of T_P is denoted $lfp(T_P)$ and $lfp(T_P) = T_P \uparrow \omega$ and captures the intended meaning of derivability of disjunctive logic programs.

Minker and Rajasekar have shown in [2] that for $\forall M \in MM(P)$. $M \models C$ if $lfp(T_P) \vdash C$. They have developed and described the proof procedures based on linear resolution which is sound and complete for answering queries from disjunctive programs.

SLI-resolution and SLIP-resolution are defined using trees as the basic representation. But for general logic program, T_P is non-monotonic. Hence there may not be a least fixed point, nor any fixed points. A model for a class of general disjunctive programs, called stratified programs, characterized by Rajasekar and Minker. They showed that for stratified program $P = P_1 \dot{\cup} ... \dot{\cup} P_n$, MS_P is a supported model of P.

For answering negative queries from disjunctive logic programs on developed the semantics for negation based on a closure operator and it is consistent with the generalized closed-world assumption.

SLINF-resolution is a proof procedure for handling negation and it is based on a concept called support for negation for an atom A, which defines a set of ground clauses which need to be logical consequence of the program to assume the negation of A.

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ASUPRA PROGRAMĂRII LOGICE DISJUNCTIVE

(Rezumat)

Se prezintă câteva generalităţi privind conceptele de bază care intervin într-un program disjunctiv: clauză, interpretare Herbrand, substituţie de răspuns, cel mai mic model de stare şi semantică declarativă şi procedurală. Pentru substituţie se prezintă o formă inedită de descriere, formă care va fi utilizată într-o lucrare viitoare.

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TEXTILE. PIELĂRIE

RODICA BUDULAN
1945–1994

In the autumn of 1994 a cruel and unjust destiny broke the life thread of Rodica B u d u l a n, BSc, PhD, Professor at the Faculty of Textile and Leather Engineering, a prestigious specialist in knitting, Head of the Department of Knitwear and Ready-made Clothing.

Born on 25th of September 1945 in Iaşi, she grew and formed herself devoted to the love for work and for accomplishing the noble mission of educating the young generations. In 1960 she graduated from the High School "G.Ibrăileanu" in Iaşi. Between 1961 to 1966 she was a student at the Faculty of Light Industry, Section of Knitwear and Ready-made Clothing of the Polytechnic Institute of Iaşi, Romania. As a student she showed exceptional qualities and acquired sound professional training, graduating from the faculty in 1966, as "head" of her series, with the highest mark, 10. For her very good results as well as for her brilliant qualities and perspectives as teacher and scientific researcher she was employed by the University, working on the Department of Knitwear and Ready-made Clothing by the tragical end of her life. She carried out her activity and formed herself as a specialist of wide national and international recognition along with prestigious professors and specialists of the Faculty and University. She acquired by competition all the stages of university career: professor's assistant in 1967, lecturer in 1977, assistant professor in 1990 and professor in 1993. She improved her professional training by obtaining in 1985 the degree of Doctor Engineer with the doctoral thesis: "Contributions to Rational Projecting of Knitwear". In 1976 she was in Germany with the Karl Mayer company for specialisation in the technology of warp knitting. She performed a scientific research work of exception which resulted in over 70 published scientific papers, 50 contracts of applied scientific research, important problems of knitting industry and which consacrated her as a distinguished specialist with widely recognised contributions to the accomplishment of programmes meant to modernize the knitting factories as well as the knitting mashines building units of Romania. Her teaching and research career was crowned by publishing 5 textbooks for students and specialists in knitting. Her personal qualities and professional competence were recognized and appreciated within University being uninterruptedly elected in the Faculty Council and in the University Senate. Between 1985 to 1990 she was Deputy Head of Department of Knitwear and Ready-made Clothing and in 1990 she was

elected and in 1991 reelected Head of the Department. All the achievements and accomplishments of university knitting teaching and scientific research in Romania undoubtedly bears the signature of Rodica B u d u l a n's outstanding personality and dedicated activity: the re-establishment of students' schooling period to 5 years, improvement of curricula, opening the Section of Technical Design and Creation in Textile-Leather, completing the new building and material basis of the section, accomplishing the documentation for the approval of the newly created sections, etc. The national recognition of her professional and scientific competence were as strong reasons for which she was asked to be member in Textile Industrial Units Administration Councils: "Elca", Cîmpina and "Siretul", Paşcani, as well as a president and scientific guide for 1st grade papers. She respected, trusted and loved students, always encouraging them for humanistic professional devotion and perfection. All younger members of the Faculty teaching staff owe a great deal to Rodica B u d u l a n's generosity and intelectual energies.

Rodica B u d u l a n's distinctive humane and professional genius and generosity will be, for ever, alive in the memory of all those who knew her, who lived and worked with her: family, collegues and student disciples alike.

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WOOL'S GRAFTING THROUGH INITIATION WITH UV RADIATIONS

III. CHARACTERIZATION BY CHEMICAL METHODS OF WOOL GRAFTED WITH ALKYL AND HYDROXYALKYL ACRYLATED-TYPE MONOMERS

BY

V. BLAŞCU, AURELIA GRIGORIU and OTILIA MÂLCOMETE

1. Introduction. In recent years, researches devoted to copolymerization grafted on textile fibers have been intensified, both for the elucidation of the theoretical aspects describing the reactions' mechanism and for the practical improvement or even assuring to them some new properties.

More than that, the behaviour, on grafting, of the fibers possessing reactive functional groups, such as cellulosic (cotton, liberian fibers, regenerated cellulose), or natural proteic ones (wool, mohair, cashmere, and silk), has been studied.

The existence of some critical properties challenged specialists to extend their grafting studies to synthetic fibres, such as: polyamidic, polyesteric, polypropylenic, polyethylenic, polyacrylnitrilic, etc., as well.

In this respect, special mention should be made of the following achievements in the field:

– elucidation of the mechanism and kinetic aspects of grafting [1], [2];

– utilization, for the process' initiation, of average (UV) and high (γ) energy radiation, i.e. grafting in solid phase [3],...,[6];

– employment of some nonconventional monomers in grafting processes, such as: ithaconic acid, 2-vinyl pyridine [8], glycidyl methacrylate [9], N-methylol acrylamide [6], dimethyl amino ethyl methacrylate [10], glycidyl acrylate [11], etc.

Our previous studies [12], [13] have analyzed the results of the investigations devoted to UV radiations-initiated grafting of some alkyl acrylated and hydroxylalkyl acrylated-type monomers, on semifine Romanian top wool of 22 type.

The present paper discusses the results obtained in the characterization – by chemical methods – of grafted wool fibers.

2. Experimental and Results

2.1. Materials and Devices. Samples of the reference fiber have been processed as described in section 2.1 of a previous paper [12].

Wool fibers grafted with alkyl acrylated and hydroxyalkyl acrylated monomers

have been obtained according to a characterization method described elsewhere [12], [13].

Out of the experimental program employed, three samples have been selected, for each monomer, for the characterization, with a minimum, average and maximum grafting degree respectively, as seen in Table 1.

Table 1

Samples of grafted wool utilized for the chemical characterization

No. of sample	Sample	No. of sample in the experimental program [12], [13]	Grafting monomer	Degree of grafting, G, %
0	Reference(Wool)	–	–	0
I.1	Wool-g-PEA	1	EA	14.16
I.2	Wool-g-PEA	7	EA	27.98
I.3	Wool-g-PEA	8	EA	37.41
II.1	Wool-g-PPA	1	PA	13.64
II.2	Wool-g-PPA	7	PA	27.58
II.3	Wool-g-PPA	8	PA	36.87
III.1	Wool-g-PBA	1	BA	13.26
III.2	Wool-g-PBA	7	BA	27.14
III.3	Wool-g-PBA	8	BA	36.45
IV.1	Wool-g-PHEA	1	HEA	13.56
IV.2	Wool-g-PHEA	7	HEA	27.37
IV.3	Wool-g-PHEA	8	HEA	36.78
V.1	Wool-g-PHPA	1	HPA	10.80
V.2	Wool-g-PHPA	7	HPA	24.73
V.3	Wool-g-PHPA	8	HPA	34.53
VI.1	Wool-g-PHBA	1	HBA	10.20
VI.2	Wool-g-PHBA	7	HBA	24.20
VI.3	Wool-g-PHBA	8	HBA	33.81

The substances employed have been the following: NaOH (p.a., Chemapol); I_2(p.a., Fluka); $Na_2S_2O_3$ (p.a., Aldrich); H_2SO_4 (p.a., Aldrich); HCl (p.a., Reactivul Bucureşti); Starch (p.a., Fluka) and Phenolphtaleine (p.a., Aldrich).

The devices utilized in the experiments have been: dessiccator with H_2SO_4 oleum 20%, for 0% RH; weighing vials; analitical balance, with a weighing precision of 4 decimal fraction; thermostate for keeping temperature constant ($\pm 0.1°C$); biurette with an interval of 0.1 mL; Würtz and Erlenmeyer bulbs equipped with a ground-glass stopper; and drying oven with thermoregulation over the 30°C and 200°C interval.

2.2. Methods of analysis. Characterization of the grafted samples made use of both quantitative (determination of the cystinic sulphur, of acid and alkaline solubility, and of tinctorial affinity) and qualitative methods (microscopic study of the acid or alkaline treated fibers, at various concentrations and temperature, determination of the dissolving time, visual appreciation of the solution obtained, analysis of the non-solved residue).

For all determinations, the wool samples, both the reference ones and these modified through grafting, have been maintained in the dessicator with 0% R.H.

up to their perfect drying, while weighings have been performed in closed vials.

2.2.1. Quantitative methods of analysis. a) *Determinations of cystinic sulphur.* In wool, sulphur is mostly occuring as cystinic, in variable (lower or higher) amounts, playing an essential role in fiber forming.

Determination of the sulphur content in the wool fiber is usually made by two methods: the gravimetric and the volumetric one.

The former method is based on the oxidation of sulphur at the SO_4^{2-} anion which, together with $BaCl_2$ shifts to $BaSO_4$ to be further determined gravimetrically [14].

The volumetric method [15] has been selected for the analysis as being more accesible and more reproducible. It is based on the release of H_2S from wool dissolved in a NaOH solution, according to the following mechanism:

$$\left.\begin{matrix}\backslash\\ /\end{matrix}\right. CH - CH_2 - S - S - CH_2 - CH \left.\begin{matrix}/\\ \backslash\end{matrix}\right. \xrightarrow{NaOH(H_2O)} \left.\begin{matrix}\backslash\\ /\end{matrix}\right. CH - CH_2 - SH + HOS - CH_2 - CH \left.\begin{matrix}/\\ \backslash\end{matrix}\right.$$

$$\left.\begin{matrix}\backslash\\ /\end{matrix}\right. CH - CH_2 - SOH \longrightarrow \left.\begin{matrix}\backslash\\ /\end{matrix}\right. CH - CHO + H_2O$$

The H_2S released represents half of the cystinic S, being titrated iodometrically in a strongly acid medium, thus hindering iodine's linking to wool's aminic groups. Iodide solution in excess is necessary for the reaction of the H_2S thus formed.

The excess iodide is titrated with natrium thiosulphate. 1mL of N/10 solution of $Na_2S_2O_3$ corresponds to 1.7 mg sulphur and, respectively, to 12 mg cystine.

For each sample, 3 determinations have been made, the average values of which are given in Table 2.

Table 2
Content of cystinic sulphur

No. of sample	Cystinic sulphur	No. of sample	Cystinic sulphur
0	3.20	IV.1	3.09
I.1	2.98	IV.2	2.99
I.2	2.82	IV.3	2.87
I.3	2.54	V.1	3.14
II.1	3.03	V.2	3.09
II.2	2.96	V.3	3.02
II.3	2.80	VI.1	3.16
III.1	3.12	VI.2	3.12
III.2	3.07	VI.3	3.06
III.3	3.00		

b) *Determination of the aminic groups.* The structure of keratin includes aminoacids with basic (aminic) groups in the lateral chain, such as: lysine, arginine, hystidine. The content of aminic groups may be determined titrimetrically, with solutions of acids [16].

Titration involves the presence of HCl in excess, non-linked to the aminic groups. Once known the initial amount of HCl, the quantity of HCl to the free aminic groups may be calculated from the following rection:

$$-NH_2 + HCl \longrightarrow N^+H_3Cl^-$$

and, implicitly weight (in grams) of the free $-NH_2$ groups in the sample subjected to analysis; finally, the percent content may be calculated.

Three determinations have been made for each sample, the results listed in Table 3 representing their average values.

Table 3
Content of Aminic Groups

No. of sample	NH_2 %	No. of sample	NH_2 %
0	2.81	IV.1	2.31
I.1	1.82	IV.2	2.12
I.2	1.60	IV.3	2.06
I.3	1.37	V.1	2.60
II.1	2.15	V.2	2.45
II.2	1.80	V.3	2.26
II.3	1.73	VI.1	2.72
III.1	2.49	VI.2	2.58
III.2	2.30	VI.3	2.39
III.3	2.17		

Table 4
Alkaline Solubility

No. of sample	S_{NaOH} %	No. of sample	S_{NaOH} %
0	8.60	IV.1	7.50
I.1	7.30	IV.2	7.45
I.2	7.06	IV.3	7.03
I.3	6.22	V.1	7.96
II.1	7.36	V.2	7.81
II.2	7.32	V.3	7.74
II.3	6.76	VI.1	8.40
III.1	7.62	VI.2	8.25
III.2	7.47	VI.3	8.02
III.3	7.05		

c) *Determination of alkaline solubility.* Wool's solubility in alkaline solutions provides information on the intensity of the modifications induced by various chemical agents upon the fiber's chemical properties.

The experimental technique selected was S m i t h and H a r r i s's test, described in literature [14], [17],...,[20].

Alkaline solubility represents the weight loss of the analyzed sample, being calculated with relation:

$$S_{NaOH} = \frac{M_1 - M_2}{M_1} \cdot 100 \qquad (\%),$$

where: M_1 – the absolutely dry weight of the sample analyzed, g; M_2 – the absolutely dry weight of the residue, g.

The results obtained are centralized in Table 4.

d) *Determination of acid solubility.* The method of L a h n and W ü r t z [15], involving treatment of the wool sample with a 4 N solution of HCl, under determined conditions of temperature, time and volume, has been applied.

Acid solubility, representing the weight loss of the dried sample, after the treatment, is calculated with relation:

$$S_{HCl} = \frac{M_1 - M_2}{M_1} \cdot 100 \qquad (\%),$$

where: M_1 – weight of the dry sample subjected to analysis, in g; M_2 – weight of the dry residue, g.

The results are centralized in Table 5.

Table 5
Acid Solubility

No. of sample	S_{HCl} %	No. of sample	S_{HCl} %
0	17.75	IV.1	16.83
I.1	16.31	IV.2	16.61
I.2	16.18	IV.3	16.21
I.3	15.80	V.1	17.06
II.1	16.43	V.2	16.71
II.2	16.20	V.3	16.50
II.3	16.12	VI.1	17.20
III.1	16.52	VI.2	16.82
III.2	16.30	VI.3	16.61
III.3	16.34		

Table 6
Exhaustion Degree of the Acid Dyers

No. of sample	E %	No. of sample	E %
0	84.3	IV.3	92.8
I.3	79.2	V.3	89.3
II.3	75.4	VI.3	87.5
III.3	73.2		

e) *Determination of tinctorial affinity.* Tinctorial affinity has been determined through dyeing with acid Red 6A (CI 16250), under the following conditions: 3% dye, 2% CH_3COOH, $M = 1 : 100$, 60 minutes, at 100°C. Percent exhaustion of the dye was calculated with relation [21]:

$$E = \frac{m_f}{m_s} \cdot 100 \qquad (\%),$$

where: m_f – dye mass in the fiber, as determined by colorimetry of the residual floats, g; m_s – dye mass in the initial floats, g.

Determinations have been performed both with the reference wool samples and with those with a maximum degree of grafting.

The results obtained are listed in Table 6.

2.2.2. Qualitative methods of analysis. Some authors [15], [20], [22], [23] recommend the application of qualitative methods for putting into evidence the modifications induced by the treatment of wool samples with acid or alkaline soliutions, at different concentrations and temperature values, as well as for the analysis of such modifications by optical microscopy or, in the case of dissolution, timing of the sample's total solubilization.

The samples' behaviour has been studied in solutions of:

– NaOH 5%, on boiling, timing of solubilization and visual estimation of the solution obtained (Table 7);

– NaOH 45%, at cold, microscopic observation, longitudinally, of the treated samples (Table 8);

– H_2SO_4 70%, at could, subsequent microscopic analysis (Table 9);

– HCl 6 N, at 115°C, subsequent study of the solution of insoluble polymer.

Hydrolysis, in solutions of 6 N HCl, was performed at 115°C, for 24 hours [24].

Table 7

Behaviour of the Wool Samples in NaOH 5%, on Boiling

Sample	Observations
0	Dissolution in 5 seconds
Samples with a minimum grafting degree I.1...VI.1	Dissolution, accompanied by slight gelling, in 10 seconds
Samples with an average grafting degree I.2...VI.2	Dissolution, accompanied by gelling, in 20 seconds
Samples with a high degree of grafting I.3...VI.3	Dissolution, accompanied by intense gelling, in 45 seconds

Table 8

Behaviour of the Wool Samples in NaOH 45%, at Cold[a)]

Sample	Observations
0	Ring shaped aspect of the fibers, as a consequence of a stronger contraction of keratin
Samples with a minimum grafting degree I.1...VI.1	More reduced contraction, comparatively with the reference fibers
Samples with an average grafting degree I.2...VI.2	A weak bending of the fibers, comparatively with their initial parallelism
Samples with a high degree of grafting I.3...VI.3	No modifications observed, comparatively with the untreated samples[b)]

[a)] An IOR optic microscope with a magnification degree ×60 has been employed, the fibers being well parallelized on the microscope's lamella.

[b)] The untreated samples have been immersed in distilled water.

Table 9

Behaviour of the Wool Samples in H_2SO_4 70%, at Cold[a)]

Sample	Observations Longitudinal microscopic aspect
0	Strongly torn scales
Samples with a minimum grafting degree I.1...VI.1	Ragged scales
Samples with an average grafting degree I.2...VI.2	Weakly ragged scales
Samples with a high degree of grafting I.3...VI.3	No ragged scales were observed

[a)] An IOR optic microscope with a magnification degree ×200 has been employed.

In the case of reference wool fibers, a clear solution is obtained while, for the wool fibers grafted in solution a resinous weight, representing the part of grafted copolymer remains. If considering the aspect of this "residue", some qualitative conclusions may be drawn as to grafting (Table 10), or a quantitative parameter, i.e. grafting's efficiency, may be calculated. Also, purification of this resinous amount through washing of the acid traces, dissolution in benzene and several reprecipitations, permits some spectral (IR), or chemical (determination of the

average molecular weight) analysis and, respectively, calculation of a polydispersity coefficient (aspects to which subsequent studies will be devoted).

Table 10

Samples Behaviour on Dissolution in a Solution of 6 N HCl

Sample	Qualitative aspect obtained
0	Clear solution
Samples with a minimum grafting degree I.1...VI.1	Weakly resinous aspect
Samples with an average grafting degree I.2...VI.2	Moderate resinous aspect
Samples with a high degree of grafting I.3...VI.3	Intense resinous aspect

3. Interpretation of Results. The observation was made that grafting induced decrease of the content of cystinic sulphur, which evidences involvement, in the reaction, of cystinic bond. Nevertheless, the decrease is quite low, so that between the reference sample (containing 3.20% cystinic sulphur) and the one possesing the highest grafting degree I.3 (containing 2.54% cystinic sulphur), the difference is of only 0.74% while, with the other samples, decrease of the sulphur content is below 0.5%.

The percent decrease of the cystinic sulphur content in grafted wool samples is correlated with the reactivity of monomers from the reaction of grafted copolymerization [12],[13].

The same phenomenon, of decreasing content of the free aminic groups, is to be observed with the samples of grafted fibers, versus the reference ones. The decreasing tendency is even more pronounced than in the case of cystinic sulphur; thus, between the reference sample (2.81% NH_2) and the one possesing the highest degree of grafting I.3 (1.37% NH_2), the difference recorded is of 1.44% while, for the other samples, the percent reduction of $\%NH_2$ varies between 1.07% and 0.1%. In this case, too, a correlation with the monomers' reactivity is established, the higher its value is, and, the closer to the optimum are the reaction conditions, the lower is the content of aminic groups.

The tests of acid and alkaline solubility evidence, by the application of classical methods, the type and degree of degradation of wool fibers as a result of various processings [15],...,[20]. However, such tests may also provide useful information on the fiber's chemical modification, mainly induced by their interaction with monomers (either in grafting reactions or during interfacial polycondensation) [18]. The obtained results evidence a slight decrease of acid solubility: 1.95% (reference sample, 17.75% and sample I.3, 15.80%) and of alkaline solubility, too: 2.42% (reference sample, 8.60% and sample I.3, 6.22%). For the other samples, the decreasing percents vary between 1.63% and 0.75%, respectively between 1.94% and 0.2%, a certain correlation with the degree of grafting being established, as follows: the higher the grafting degree, the corresponding decrease of the acid and

alkaline solubility occurs.

As to the tinctorial affinity, it evidences the modifications appearing in the fibers' chemical structure, outlining grafting's prevailing character in the fiber's external layers. Also, a decreased adsorption of the acid dye may be observed, comparatively with the reference sample, in the case of wool samples grafted with hydrophobic monomers, as correlated, too, with the decrease of the aminic groups, in parallels with a slight increase of tinctorial affinity, comparatively with the reference sample, for the samples grafted with hydrophilic monomers.

A good correlation has been observed between the monomers' reactivity [12], [13] during grafting and the grafted samples' tinctorial affinity.

Qualitative methods offer rapid information on the chemical modifications having occured in keratin through the reaction of grafting. The qualitative differences observed with the grafted samples, comparatively with the reference fibers, are even more evident, the higher is the grafting degree.

4. Conclusions. The methods of chemical (both quantitative and qualitative) analysis applied evidence the modifications suffered by the wool fibers grafted through initiations with UV radiations, with monomers of alkyl and hydroxyalkyl acrylated monomers.

The experimental results obtained permit the conclusion that the reaction of grafting involves the presence of both cystinic bond and free aminic groups. Also participation in the reaction of other groups from keratin's constituting α-aminoacids, by the formation of free radicals under the action of UV radiations, is not excluded.

Cystinic sulphur determinations permit to conclude that their participation is quite low, having no influence on the fiber's "architectonic" structure, while participation to the reaction of the aminic groups and of other functional groups of keratin permits restoring of the previously affected reticulations to the inter- and intrachain cystinic bonds, and even their increasing, through grafting reactions.

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GREFAREA LÂNII PRIN INIŢIERE CU RADIAŢII UV

III. Caracterizarea prin metode chimice a lânii grefate cu alchil şi hidroxialchil acrilaţi

(Rezumat)

Se prezintă mai multe metode chimice de analiză, cantitative şi calitative, a fibrelor de lână românească sort 22 grefate cu şase monomeri cu structură acrilică.

Se analizează rezultatele obţinute din numeroasele metode abordate, corelându-le şi trăgând concluzii adecvate.

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WOOL'S GRAFTING THROUGH INITIATION WITH UV RADIATIONS

IV. CHARACTERIZATION BY PHYSICAL METHODS OF WOOL GRAFTED WITH ALKYL AND HYDROXYALKYL ACRYLATED-TYPE MONOMERS

BY

AURELIA GRIGORIU, V. BLAŞCU and OTILIA MÂLCOMETE

1. Introduction. Wool has been subjected to several reactions for the chemical modification of its fiber structure, for the improvement of some properties such as: contraction and thermal stability, tinctorial capacity, resistance to chimical agents etc. [1],...,[5].

An important category of wool's chemical modifications refers to its interactions with monomers or organic substances with reactive functions, for the generation of macromolecular compunds. Therefore, by the application of various polymerization or polycondensation techniques on the fiber's surface there may be deposited synthetic polymers such as: butadienic or styrene-butadienic rubber, butadiene-unsaturated ketones copolymers, polyethene, polypropene, epoxidic resins, polysiloxanes, polyurethanes, etc.

During the development of the chemical processes, covalent bonds may be formed between the polymer and keratin; in such cases, the polymer is grafted on keratin.

During grafting, some of keratin's chemical functions are being activated, free radicals, which react with the grafting monomers, being thus obtained in the polypeptidic chain.

The technique of vinylic monomers grafting on fibers of Romanian wool represented one of our scientific concerns, the results of our laboratory investigations having been discussed [6],...,[11].

In present study analyzes the results obtained in the physical characterization of wool grafted with alkyl- and hydroxyalkylacrylated- type monomers [10], [11].

The physical methods employed have been the following: study of the modifications of the cross dimension through diameter and fineness indexes; study of water absorption through hysteresis curves; swelling anisotropy and density determinations.

2. Experimental.

2.1. Material and devices. Determinations of diameter were made on a Karl Zeiss Jena-type Lanameter with a magnification degree ×500 [10]. Weighings were made on an analytical balance with a precision of four decimal fractions, in weighing vials.

Media with various relative humidities (from 0% RH up to 100% RH) have been obtained in desiccators, on employing H_2SO_4 oleum 20% and H_2SO_4 solutions with well established concentrations. H_2SO_4 p.a. with ρ=1.83 g/mL was employed.

Determinations of swelling anisotropy involved measurements on an ocular micrometer attached to an IOR-type optic microscope, with a magnification degree ×200. For the obtainment of cross sections, the fibers have been included in boiled crib, then cut with a manual microtome.

Determinations of density were made in two variants: with a 50 mL picknometer, equipped with lateral capillary and thermometer and with double walls density gradient column.

Toluene, the ethylic alcohol and carbon tetrachloride, organic substances, p.a., have been employed in the determination of fibers' density.

The density gradient column is a graduated tube, equipped with ground-glass stopper, 65 cm in length and 5 cm in diameter, and with double walls for thermostating. Of special importance are the spherical glass floats, calibrated, made of reburnt glass, covering the 1.1500-1.4000 density interval, and distributed uniformly over it. Areometers are also necessary, to cover the density interval with a minimum division of 0.001, besides a siphon or a pipette system for filling the gradient column.

Column's thermostating made use of a thermostate, on maintaining the temperature constant at ±0.1°C.

The samples of wool, both the reference and the grafted ones, have been prepared for experiments according to a method of our own [10], [11], while codification is the same given in a previous paper [12].

2.2. Working method. Determination of the fibers' diameter was made as recommended by ISO 137 [13] for conditioned fibers (65% RH and 22°C). For a trust interval of ±2% and a probability of 95%, 600 measurements per sample are required.

Fineness in Tex system was determined gravimetrically, by segmentation of a sample of 20 mg well paralleled and smoothed out fibers, at a 20 mm length. Numbering of the sectioned fibers in the sample and establishing of weight permit calculation of fineness with relation:

$$\text{Tex} = \frac{m}{n \cdot l},$$

where: m – weight of the sectioned fibers, [mg]; n – number of the sectioned fibers; l – sectioning length, 20 mm.

Fineness was also determined from the samples' average diameter and density with relation:

$$\text{Tex} = \frac{\pi}{4} \cdot \overline{d}^2 \cdot \rho,$$

where: $\overline{d}$ – average diameter of the wool sample, [μm]; ρ – fibers' density, as determined by the method of the density gradient column, [g/mL].

The sorption hysteresis curves have been plotted through 7 points, both for absorption and desorption. The experimental points have been obtained from the determination through weighing, of fibers' humidity at 7 values of air relative humidity, as follows: φ=0; 10; 35; 50; 65; 90 and 100% RH.

The amounts of H_2SO_4 oleum 20%, H_2SO_4 (ρ=1.83 g/mL) and distilled water necessary for the preparation of solutions in desiccators were calculated as recommended in literature [14].

Calculation of fibers' relative humidity was made with relation:

$$U = \frac{M_1 - M_2}{M_2} \cdot 100, \qquad [\%],$$

where: M_1 – weight of the wool fibers established at different φ values, [g]; M_2 – weight of the perfectly dried wool fibers, when φ=0% RH, was considered as constant: M_2=0.4000 g.

Swelling anisotropy was determined by measuring the fibers' longitudinal and cross diameters, in conditioned state (65% RH, 22°C) and by immersion in water, the fibers being sectioned at an about 200 μm length, by means of a microtome. For the calculation of swelling anisotropy, the following relation has been employed:

$$A = \frac{\Delta d}{\Delta l},$$

where: A – swelling anisotropy; Δd – increase in diameter, by swelling: $\Delta d = \overline{d} - \overline{d}_0$, [$\mu$m]; Δl – increase in length, by swelling: $\Delta l = \overline{l} - \overline{l}_0$, [$\mu$m]; $\overline{d}_0$, $\overline{l}_0$, $\overline{d}$, $\overline{l}$ – average dimensions before and after swelling of the sectioned fibers, [μm].

The swelling degrees have been also calculated:

– in length, $U_l = (\Delta\overline{l}/\overline{l}_0) \cdot 100 = [(\overline{l} - \overline{l}_0)/\overline{l}_0] \cdot 100$, [%];

– in thickness, $U_d = (\Delta\overline{d}/\overline{d}_0) \cdot 100 = [(\overline{d} - \overline{d}_0)/\overline{d}_0] \cdot 100$, [%];

– in volume, $U_V = (\Delta\overline{V}/\overline{V}_0) \cdot 100 = [(\overline{d}^2\overline{l} - \overline{d}_0^2\overline{l}_0)/\overline{d}_0^2\overline{l}_0] \cdot 100$, [%].

The wool fibers being approximately cylindrical in shape, the fiber's volume is that of a cylinder.

Density determinations made use of two methods, as follows:

– the picknometric method, using toluene as a picknometric liquid, according to literature data [16];

– density gradient column, involving the pair of liquids: ethylic alcohol p.a. (ρ=0.80 g/mL) and carbon tetrachloride p.a. (ρ=1.59 g/mL) [15], [16].

Although the literature of the field makes mention of other liquids, too (such as aqueous solutions of various anorganic salts in different concentrations: KI, $Ca(NO_3)_2$, NaBr) [16], [17], we have selected, for the density domain interesting us

(i.e. 1.10-1.40 g/mL), having also prolongued stability, the ethylic alcohol-carbon tetrachloride system of liquids, in spite of their higher volatility and of the difficulties they show during utilization. Our selection was based on the fact that such organic liquids are inert, comparatively with keratin and with grafted polymers, they do not induce fibers' swelling, dimensional modifications, degradation, a.s.o., which would affect fibers' flotation in the column and thus, would denaturate the experimental results.

Preparation of the density gradient column was made according to literature [17].

The calibration curve obtained by means of the float is plotted in Fig.1 (scale 1:20), also, on having a single inflexion point, it meets the requirements [16].

3. Results and discussion.

3.1. Determination of diameter. 600 measurements of diameter were made for each sample, followed by their registration, devision into classes of 2 μm thickness and their statistico-mathematical interpretation.

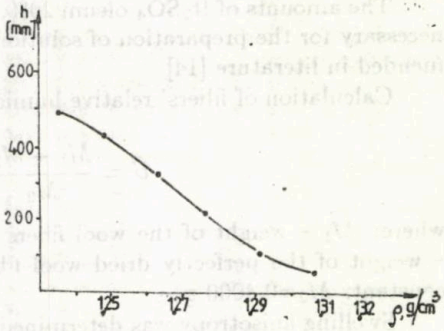

Fig. 1.– Calibration curve of the gradient column.

The average diameter is calculated with relation:

$$\overline{d} = \frac{d_i \cdot n_i}{n_i}, \qquad [\mu m],$$

where: $\overline{d}$ – average diameter of the sample, [μm]; d_i – average diameter of the sample, [μm]; n_i – absolute frequency (number of fibers in a class).

Also, there are calculated the average square deviation $\sigma = [(d_i - \overline{d})^2 \cdot n_i]/n_i$, [$\mu$m], and the variation coefficient $C_V = (\sigma/\overline{d}) \cdot 100$, [%].

The results obtained are presented in Table 1.

The values of average diameter obtained in the statistico-mathematical interpretations of the 600 determinations per sample are quite close to those of average diameter obtained as aritmetic means, as presented in other studies of ours [10], [11], a deviation of maximum 1% being possible, which is part of the experimental errors accepted.

By grafting, dispersion (average square deviation) decreases proportionally with the grafting degree, the same evolution being observed for the variation coefficient.

The explanation lies in a more pronounced uniformization of the fineness properties, in the case of grafted samples, which is also evidenced by a lower basic opening of the distribution curves, the values' "scattering" being lower, the higher the grafting degree is.

3.2. Determination of the fibers' fineness indices. The values of fineness, expressed as Tex, obtained by the two mentioned methods, are listed in Table 2.

Table 1

Values obtained from the statistico-mathematical interpretation

No. of sample	$\bar{d}$ μm	σ μm	C_V %	No. of sample	$\bar{d}$ μm	σ μm	C_V %
0	22.56	6.18	23.60	IV.1	24.90	5.41	22.42
I.1	25.70	5.23	22.02	IV.2	27.87	5.30	22.07
I.2	28.46	4.97	21.70	IV.3	31.20	5.06	21.90
I.3	31.71	4.72	21.34	V.1	24.01	5.71	22.95
II.1	24.87	5.29	22.18	V.2	25.10	5.63	22.83
II.2	29.60	5.16	21.97	V.3	29.70	5.40	22.66
II.3	31.42	4.94	21.85	VI.1	23.14	5.90	23.40
III.1	24.60	5.46	22.70	VI.2	24.92	5.84	23.16
III.2	27.72	5.37	22.57	VI.3	29.56	5.65	22.77
III.3	29.97	5.28	22.11				

Table 2

Values of the fineness index

No. of sample	Tex by the gravimetric method	Tex from diameter and density	No. of sample	Tex by the gravimetric method	Tex from diameter and density
0	0.538	0.522	IV.1	0.590	0.593
I.1	0.623	0.618	IV.2	0.615	0.610
I.2	0.640	0.643	IV.3	0.631	0.627
I.3	0.690	0.684	V.1	0.540	0.545
II.1	0.618	0.615	V.2	0.562	0.567
II.2	0.631	0.638	V.3	0.578	0.582
II.3	0.645	0.637	VI.1	0.542	0.541
III.1	0.577	0.580	VI.2	0.543	0.548
III.2	0.602	0.592	VI.3	0.558	0.555
III.3	0.600	0.603			

Slight differences exist between the values of fineness obtained by the two methods, which confirms the results' reproducibility. For each sample, the calculation of fineness made use of the density value determined experimentally, by the method of density gradient column.

Increase of the grafting degree induces a decrease in fineness, which was observed, as well, from diameter determination. Decrease of fineness by about 5% is not so drastical to affect fibers' subsequent technological processing or to change their final destination (the chemically modified fibers still remaining as reference fibers, according to 22 type).

Although the increase in diameter, induced by grafting, is more considerable up to 30%, decrease in fineness is less "abrupt", as a result of the decreasing density of the grafted fibers, comparatively with the reference sample.

3.3. Determination of the sorption curves. The fibers' capacity of sorption water

vapours, along with diffusion of liquid water in the fibrous substrate represent essential characteristics of the physico-chemical processes and of their physiological and mechanic properties, too.

Phenomena such as water vapour sorption and liquid water diffusion depend firstly on keratin's chemical structure, weight and polarity of the functional groups and, secondly, on the supramolecular and hysto-morphological structure of the wool fibers [4].

In the processes of water vapour sorption by the wool fibers, three stages have been identified, in which the water molecules are fixed in the fiber. In the first stage, water molecules are bound to the free polar groups from the lateral chains, through hydrogen bonds, which is accompanied by a considerable release of heat, after which new water molecules are fixed to the polar groups from the main chain, involving a diminished heat release, which constitutes the hydratation water.

In a third stage, in conditions of humidity in express, the water molecules addition in a labile form in the structural spaces having microcavities, thus forming the capillarity (swelling) water [18].

In the process of water's desorption from the fibers, the phenomenon is observed as occurring similarly with the sorption one, while the desorption curve is situated over the sorption one. The occurence of hysteresis with hygroscopic fibers indicates that the fiber retains an additional amount of water, comparatively with the desorption curve, as part of water, molecules, strongly fixed on the polymer, remain in the fiber's structure, thus forming the "bound water", unlike the "free water", which is easily released [19].

Analysis of wool fibers' sorption isotherms permits to determine the water vapours' accessibility in the fiber, by calculating the hysteresis and, respectively, the "relative hysteresis" for the air's relative humidity of 65% RH and the temperature of 22°C, with relation:

$$H_r = \frac{U_d - U_a}{U_a} \cdot 100, \quad \% \quad \text{or} \quad H'_r = \frac{U_d - U_a}{U_d} \cdot 100, \quad \%,$$

where: U_d – the water content from the fiber on the desorption curve, %; U_a – the water content from the fiber on the sorption curve, %.

Planimetering of the hysteresis surfaces from the sorption curves offers even more detailed and complete information, which permits a better interpretation of the multiple aspects characterizing the sorption phenomenon.

The results obtained are given in Table 3.

Analysis of the wool fibers' sorption, the following observations may be made:

– increase of hysteresis and of the hysteresis surface with the fibers grafted with hydroxyalkyl acrylated monomers (samples IV, V and VI);

– decrease of these sorption parameters with the fibers grafted with alkyl acrylated monomers (samples I, II and III);

– increase of the sorption parameters is proportional with the increase of the degree of grafting hydroxyalkyl acrylated monomers, while their decrease is in-

Table 3
Values of the Sorption Hysteresis

No. of sample	h %	U_a %	U_d %	H_r %	H'_r %	Hyst. surf. mm^2
0	2.1	16.0	18.1	13.12	11.60	552
I.1	1.5	14.0	15.5	10.71	9.67	492
I.2	1.2	13.1	14.3	9.16	8.39	612
I.3	1.0	12.8	13.8	7.81	7.24	270
II.1	1.6	14.8	16.4	10.81	9.75	600
II.2	1.3	13.7	14.6	9.48	8.90	468
II.3	1.1	12.7	13.0	8.66	8.46	288
III.1	1.8	15.1	16.9	11.92	10.65	600
III.2	1.4	13.5	14.9	10.37	9.39	468
III.3	1.1	12.8	13.9	8.59	7.91	288
IV.1	2.7	17.3	21.0	15.60	12.85	750
IV.2	3.6	18.0	21.6	20.00	16.66	1110
IV.3	4.2	18.8	23.0	22.34	18.26	1260
V.1	2.6	17.2	19.8	13.37	13.13	720
V.2	2.8	17.5	20.3	16.00	13.79	870
V.3	3.8	18.4	22.2	20.65	17.11	1080
VI.1	2.4	16.4	18.8	14.63	12.76	816
VI.2	2.7	17.3	21.0	15.60	12.85	870
VI.3	3.6	19.0	22.6	18.90	15.92	1056

versely proportional with the increase of the degree of grafting with alkyl acrylated monomers;

– size of the hydrocarbonated chain influences sorption, as well, consequently, with its increase, sorption hysteresis decreases.

As seen from Table 3, the evolution of h, H_r and H'_r has the same direction, while the size of the hysteresis surface evidences the strength of the links created between fiber and the water molecules.

The explanation for the water molecules' sorption, initially more rapid and slower with increasing humidity, was first provided by F.T. P e i r c e and J.B. S p e a k m a n [4]. From a quantitative viewpoint, during sorption, the wool fibers bind, in the beginning, a higher amount of water (the hydratation water) while, from the viewpoint of the process' kinetics, the sorption rate increases slowly over the 40%-70% domain of relative humidity, which is followed by another rapid increase, up to saturation (100% RH).

Such sorption aspects may be explained through keratin's macromolecular structure, as well as in wool's supramolecular (i.e., crystalline-amorphous) structure; more recently, a new theory, backed up by mathematical arguments, devoted to the sorption–desorption and multilayer diffusion phenomena occuring in wool fiber, has been put forth [21].

3.4. Determination of Swelling Anisotropy. The experimental results, representing

Table 4

Values of Swelling Anisotropy Recorded with the Samples Analyzed

No. of sample	Swelling in length, U_l, %	Swelling in diameter, U_d, %	Swelling in volume, U_V, %	Swelling anisotropy, A
0	1.67	16.40	38.23	9.82
I.1	1.43	15.86	36.26	11.09
I.2	1.26	15.30	35.41	12.43
I.3	1.10	14.92	34.36	13.56
II.1	1.52	16.02	33.14	10.53
II.2	1.34	15.80	32.06	11.73
II.3	1.28	15.52	31.08	12.12
III.1	1.50	15.95	32.40	10.60
III.2	1.31	15.63	31.16	11.93
III.3	1.27	15.48	30.96	12.18
IV.1	1.82	16.90	42.30	9.28
IV.2	1.94	17.20	43.50	8.86
IV.3	2.06	17.74	44.14	8.61
V.1	1.93	16.53	41.06	8.56
V.2	2.10	16.93	41.93	8.06
V.3	2.16	17.20	42.13	7.96
VI.1	1.87	16.00	39.28	8.55
VI.2	1.90	16.02	40.12	8.43
VI.3	2.04	16.40	41.12	8.03

average values of 30 determinations/sample are presented in Table 4.

On analyzing the values thus obtained, the conclusion may be drawn that, in spite of the contradictory character of the literature data, in the case of the reference samples, the values are closer to those given in other studies.

On following the swelling degrees in both length and diameter of the grafted fibers, it was observed that the values generally decrease for the samples grafted with hydrophobic monomers (samples I, II and III), and increase for those grafted with hydrophylic monomers (samples IV, V and VI), comparatively with the reference. The variations recorded are more significant the higher is the grafting degree. The same behaviour may be observed with the degree of swelling in volume. Nevertheless, the swelling anisotropy has higher values for the samples grafted with hydrophobic monomers, comparatively with the reference sample, the situation being reversed for the samples grafted with hydrophylic monomers. A possible explanation would lie in the manner in which the grafted polymers interact with the fiber's morphological structure, which affects the amorphous-cristalline structure.

3.5. Determination of fibers' density. Apart from the picknometric method and the method of gradient column density, the density of the wool fibers, both the reference and the grafted ones, has been calculated theoretically, as well. Consequently, if the wool and the grafted polymer are separated in two phases in the grafted fiber, without destroying the α-crystallites, the weights of the two parts are additive,

equations for the calculation of the grafted fibers density being proposed. One of the equations of this type is:

$$\frac{1}{\rho} = \frac{1-x}{\rho_W} + \frac{x}{\rho_P},$$

where: ρ, ρ_W, ρ_P are the density values of the grafted fibers, of unmodified wool and of the subsequently isolated grafted polymer; x – polymer fraction, $x = G/(G+100)$, G – degree of grafting, [%].

The fraction of grafted polymer has been calculated with the values of the grafting degrees. Further on, having the values of ρ_W and ρ_P for the six grafted polymers, theoretical values have been also obtained for the density samples taken into study.

Table 5 lists the experimentally determined obtained by the two methods and also the calculated densities.

The experimental values represent averages of 3 determinations/sample.

Table 5
Fibers' Density

No.of sample	$\rho_{picknometric}$ g/mL	ρ_{column} g/mL	$\rho_{theoretical}$ g/mL
0	1.3024	1.3017	1.3010
I.1	1.2897	1.2887	1.2876
I.2	1.2772	1.2762	1.2730
I.3	1.2457	1.2463	1.2440
II.1	1.2912	1.2884	1.2862
II.2	1.2764	1.2743	1.2716
II.3	1.2504	1.2471	1.2448
III.1	1.2965	1.2930	1.2912
III.2	1.2892	1.2870	1.2863
III.3	1.2662	1.2611	1.2543
IV.1	1.2946	1.2921	1.2895
IV.2	1.2833	1.2802	1.2746
IV.3	1.2564	1.2516	1.2487
V.1	1.2938	1.2909	1.2883
V.2	1.2876	1.2835	1.2803
V.3	1.2713	1.2690	1.2652
VI.1	1.2976	1.2932	1.2920
VI.2	1.2893	1.2836	1.2817
VI.3	1.2770	1.2719	1.2696

Analysis of this results permits the conclusion that the samples' density decreases with the increase of the grafting degree. The nature of the grafting monomer exercises no significant influence. The grafted polymeric phase has a lower density,

ranging between 1.10 and 1.17 g/mL comparatively with the values recorded fpr keratin (of 1.30 – 1.32 g/mL), which explains the density modifications induced by grafting.

The density values of the samples obtained analitically, from the calculations, evidence the same evolution, comparatively with the grafting degree, as the experimental ones, the differences being more pronounced for various degrees of grafting.

Slight differences have been observed between the density values obtained by the experimental methods, in all cases those calculated by the gradient column method being lower than the values obtained by the picknometric one. Such differences may be explained through the experimental errors, nevertheless, if considering their sense, i.e., $\rho_{\text{picknometer}} - \rho_{\text{column}} > 0$, which is the same for all samples, and also the closer values of ρ_{column} to $\rho_{\text{theoretical}}$, the conclusion may be reached that the method of the density gradient column assures more precise values. This may be caused by a more prolongued keeping of the sample in the immersion liquid (24 h at constant temperature). The method's precision is being correlated with the amplitude of the immersion liquid's diffusion in the fiber. As diffusion is a slow phenomenon, the higher duration (24 h) of sample's maintaining in the density column permits a more correct determination of the fiber's real volume, comparatively with that determined picknometrically, for which the immersion duration is more reduced (30 min). The results obtained for wool agree, generally, with the porosity studies developed on the Romanian PAN, Melana fibers [23].

Graphical plotting of $1/\rho = f(x)$ for the experimentally obtained values (Fig.2) evidences a good correlation of the experimental values with the ideal line, comparatively with Fig.3, which represents the results in the same manner, versus the ideal line of another grafting system, namely: wool-methyl methacrylate, redox initiation LiBr-$K_2S_2O_8$ [21].

In short, the assertion may be made that the gradient column method led to results with the lowest experimental error; therefore, it is recommended, as well, in studies of fibers' structure (alongwith X ray diffraction), for the establishment of the crystallinity index (I_c) and of the orientation degree (G_0).

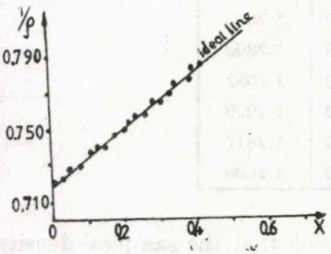

Fig. 2.– Relation $1/\rho$ as a function of x for the samples grafted through initiation with UV radiations.

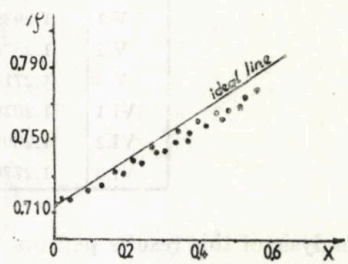

Fig. 3.– Relation $1/\rho$ as a function of x for the redox grafted wool samples [22].

4. Conclusion. Based on the information acquired from the multiple physical methods for the characterization of Romanian semi-fine wool grafted with alkyl and hydroxyalkyl acrylated monomers, the general conclusion may be drawn, that the grafting reaction affected the fibers' structure. Consequently, grafting occurs, too, inside the fiber and not only on its surface, as mentioned in several studies.

The physical methods of analysis applied demonstrate that no intense destruction of the fibers modified chemically through UV grafting occured, comparatively with the degradations caused by graftings with either redox systems or strongly oxidative agents. Actually, in many cases, in view of a redox initiation of grafting the wool fiber is predegradeted with various chemical agents, such as: natrium sulphide, thyoglycolic acid, etc., which is not necessary in the reaction systems employed by us.

On the contrary, according to our own grafting techniques, and also as a result of the monomers utilized, some of the fibers' properties are improved. In the case of hydroxyalkyl acrylated monomers, hydrophilicity is increased, while the sorption-desorption equilibrium is favourably modified.

For all the six monomers utilized in grafting, the results of the physical methods of investigation have evidenced improvement of swelling anisotropy and decreases of fibers' density, comparatively with the reference fibers.

As to the fineness of the grafted fibers, it decreases, comparatively with the reference, but not as pronouncedly as in other grafting systems, presented in literature, also, the thickening degree of the fibers grafted by us would not affect their subsequent processability.

In several cases, for the obtainment of more complete data and for a quicker and more direct reaching of conclusions, two or even three variants of the same physical method of investigation have been considered, the results obtained being then compared carefully.

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GREFAREA LÂNII PRIN INIŢIERE CU RADIAŢII UV
IV. Caracterizarea prin metode fizice a lânii grefate cu monomeri de tip alchil şi hidroxialchil acrilaţi

(Rezumat)

S-a efectuat un studiu complex, prin mai multe metode fizice de analiză, cu diverse variante ale acestora, a fibrelor de lână grefate cu monomeri de tip alchil şi hidroxialchil acrilaţi. Sunt prezentate proprietăţile fizice ale fibrelor modificate chimic comparativ cu cele ale martorului.

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Secţia VIII
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WOOL'S GRAFTING THROUGH INITIATION WITH UV RADIATIONS

V. MECHANICAL CHARACTERIZATION OF WOOL GRAFTED WITH ALKYL AND HYDROXYALKYL ACRYLATED MONOMERS

BY

OTILIA MÂLCOMETE, V. BLAŞCU and AURELIA GRIGORIU

1. Introduction. The wool fiber has been considered among the first for industrial utilization, having a dominant position among the textile raw materials, mainly in the period in which fibers' processing was predominantly manual.

The top position, as to fiber consumption for textile processing, hold, both in the past and nowadays, by wool, is mainly due to its multiple favourable properties. Nevertheless, in time, some shortcomings of wool have been observed [1],...[5] and, consequently, attemps were made at eliminating or, at least, diminishing them [2], [3].

Due to is very complex chemical and histo-morphological structure [2], [3], [6], [7], wool has always permitted numerous structural modifications, in view of improving fiber's quality. One of the largely applied methods in such cases is the chemical one, which removes wool's sensitivity to the action of insects and microorganisms, improves dimensional stability, filling capacity, as well as the physico-mechanical and chemical properties [1],...,[7].

Among the modern methods of wool fibers' chemical modification, that of grafting of macromolecular compounds on the fiber's surface or inside it is widely applied.

When macromolecular compounds grafted on keratin are obtained, the process' initiation is that usually applied in macromolecular chemistry. The mechanism of wool's grafting is generally radicalic. The free radicals in the polypeptide chains have been obtained either by classical (with peroxides [8], [9], redox systems [10],...,[12]) or by non-conventional metods (irradiation [13], [14], UV radiations [15], [16], with effluents [17], [18]) or by strongly oxidative agents, such as periodate, ceric or permanganic ions, etc. [19],...,[21].

Investigations of our own involved redox system [3], [22] or non-conventional initiations [17], [18], [23], [24]. The recent results we obtained in UV initiated grafting of Romanian semifine wool with alkyl and hydroxyalkyl acrylated monomers have been published [23], [24]. The grafted samples were subjected to multiple structural, both chemical and physical analyses, the results being partially com-

municated [25], [26].

The present study is devoted to the analysis of the mechanical properties of fibers modified through grafting with the above-mentioned monomers, in correlation with the results obtained with reference samples.

2. Experimental. Materials, devices and methods. Studies were made on both unmodified fibers and fibers modified with the 6 monomers. Codification, obtainment and preparation of samples being discussed in previous papers [23],...,[25].

Fiber's behaviour to traction, up to breaking, was studied on conditioned samples (65% RH, t=22°C), on employing a Fafegraph dynamometer, concomitantly with recording of the load – relative elongation curves ($P - \varepsilon$). The fibers have been pre-tensioned with a constant decreaping load (P_d=0.22 cN/fiber), the tests performed involving fiber's stressing to stretch, for a constant rate of deformation increase.

30 curves have been plotted for each sample, for better evidencing the three regions characterizing the wool fibers, namely: the elasticity, the flow and, respectively, the past-flow (breaking) region.

Interpretation of the curves was made by the method of bisectrices (Coplan) [2], [27], the following mechanical parameters being established:

– initial modulus of elasticity, E_I (cN/tex), form the curve's initial slope, for ε=1%:

$$E_I = \frac{\sigma}{\varepsilon(1\%)} \cdot 100$$

– Viscoelastic modulus of flow, E_{II} (cN/tex), calculated with relation:

$$E_{II} = \frac{\sigma_c - \sigma_e}{\varepsilon_c - \varepsilon_e} \cdot 100$$

– Proportionality limit: P_p (cN/fiber), σ_p (cN/tex), ε_p (%);

– Elasticity limit: P_e (cN/fiber), σ_e (cN/tex), ε_e (%);

– Flowing limit: P_c (cN/fiber), σ_c (cN/tex), ε_c (%);

– Breaking limit: P_r (cN/fiber), σ_r (cN/tex), ε_r (%).

Curves' planimetering with a Salmuiraghi planimeter permitted to establish the specific mechanical work of deformation up to breaking, L_{ms} (cN/tex).

Fibers' behaviour to friction was determined on a torsion balance, especially modified to this end [28]; the coefficients of static (μ_s) and dynamic (μ_d) friction were determined for fiber on fiber (f/f) and, respectively, fiber on metal friction (f/m), by the method of fiber's friction on cylindrical surface, ei-

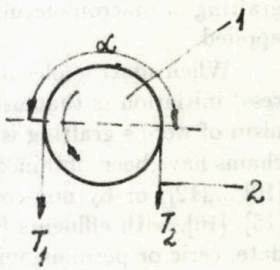

Fig. 1.– Schematic representation of the determination of fibers' friction coefficient, *1* – friction body; *2* – fiber.

ther metallic or covered with a layer of fibers oriented parallel to the cylinder's axis (Fig.1).

The tension inside the fiber is measured with a torsion balance.

On conditions of dynamic regime, friction occurs both in the direction of the scales, and in opposite direction.

The friction coefficient was calculated with Euler's relation: $\mu = \frac{1}{\alpha} \ln \frac{T_2}{T_1} = \frac{1}{\pi} \ln \frac{T_2}{T_1}$.

3. Results and Dicussion. The values of the mechanic parameters in the load-relative elongation curves are given in Table 1; they represent the average values of 30 determinations.

Their improvement, comparatively with the reference fiber, may be observed. More significant increases are recorded by the breaking load, in parallels with the increase of the grafting degree. No differentiations are observed as to fibers' tenacity, versus the grafting monomer, being known that it is only the degree of grafting that influences this parameter.

Increase of the grafting degree causes a decrease of the flow limit values, and a slight increase of the elasticity and proportionality limits.

The initial modulus of elasticity increases slightly for the grafted samples, comparatively with the reference, the same evolution being recorded by the flowing modulus (E_{II}).

The specific mechanical work of deformation up to breaking, in the case of grafted samples, comparatively with the reference, increases proportionally with the degree of grafting.

Interpretation of the modifications occuring in both grafted and reference fibers should consider the structural modifications either macromolecular or morphological level, taking place in the substrate for various values of the stress loads.

In the Hookian region, in which the applied load is proportional with the fiber's extension (Fig.2), fiber's elongation is attributed to the shifting of the polypeptidic chains one to another, accompanied by breaking of the weak interchain bonds (hydrogen bonds, van der Waals forces, etc.); this region of the curve describes fiber's elastic deformation.

In region II, where the 5% elongation is exceeded, stretching of the polypeptidic chains occurs, while α-keratin begins its transformation, an intermediate stage occurring between the forms of α- and β-keratin. The weak bonds are broken and, possibly, if stretching occurs very quickly, the process is, under certain conditions, partially reversible.

Over a relative extension of about 20%, a new inflexion point appears on the curve, the load increases more than extension, the explanation being found in stressing of new, more intense chemical bonds, opposing to the stretching of polypeptidic chains. These links are both electrovalent and covalent, among them, cystinic bridges or other reticulation links play a special part.

The results of dynamometric measurements may be interpreted, too, with the structural model of the wool fiber suggested by Feughelman and Dobb [29],

Table 1

Values of the Mechanical Parameters from the Load-Relative Elongation Curves

No. of sample	Initial modulus of elasticity E_I cN/tex	Viscoelastic modulus of flow E_{II} cN/tex	Proportionality limit			Elasticity limit			Flowing limit			Breaking limit			$\frac{\varepsilon_r}{\sigma_r}$	L_{ms} cN/tex
			P_p cN/fib.	σ_p cN/tex	ε_p %	P_e cN/fib.	σ_e cN/tex	ε_e %	P_c cN/fib.	σ_c cN/tex	ε_c %	P_r cN/fib.	σ_r cN/tex	ε_r %		
0	377.03	20.68	5.92	11.34	3.96	7.04	13.48	4.73	9.24	17.70	25.10	12.40	23.75	26.80	1.14	4.83
I.1	402.10	22.23	6.52	10.74	4.24	7.94	12.90	5.08	10.14	17.35	27.20	17.70	22.42	26.61	1.40	5.14
I.2	418.14	22.78	6.70	10.68	4.62	8.02	12.77	5.11	10.26	16.40	27.93	23.06	22.10	27.50	1.53	5.20
I.3	421.62	24.37	6.83	10.28	4.73	8.16	12.28	5.18	10.37	15.61	28.36	25.17	21.15	30.11	1.62	5.37
II.1	400.38	21.97	6.36	10.91	4.09	7.67	12.90	5.03	10.02	17.28	27.03	17.00	22.40	26.10	1.36	4.98
II.2	410.40	22.21	6.54	10.86	4.16	7.82	12.81	4.97	10.16	16.83	27.70	22.74	22.31	27.71	1.50	5.07
II.3	414.06	24.16	6.60	10.54	4.25	8.04	12.73	4.92	10.22	15.81	28.21	24.64	21.73	30.15	1.58	5.25
III.1	393.24	22.64	5.94	11.20	3.99	7.38	13.23	4.75	9.63	17.46	26.37	16.50	22.90	27.18	1.28	4.92
III.2	405.24	23.01	6.03	11.06	4.03	7.47	13.21	4.80	9.79	17.05	27.16	21.78	22.65	26.55	1.27	4.97
III.3	411.13	23.68	6.14	11.11	4.10	7.61	13.07	4.78	9.92	16.41	27.72	23.80	22.04	29.72	1.35	5.10
IV.1	397.15	21.64	6.10	11.20	4.02	7.57	13.16	4.74	9.83	17.39	26.80	16.85	22.81	25.25	1.30	5.00
IV.2	408.16	23.78	6.18	10.96	4.08	7.70	13.04	4.80	9.97	16.82	27.45	23.30	22.52	27.50	1.32	5.04
IV.3	416.36	24.02	6.25	11.04	4.18	7.84	12.95	4.83	10.16	16.03	28.05	24.44	21.87	29.32	1.44	5.18
V.1	390.46	21.12	5.95	11.26	3.97	7.18	13.18	4.75	9.48	17.60	26.14	14.02	23.00	24.91	1.20	4.87
V.2	402.13	22.85	5.98	11.08	4.00	7.30	13.08	4.75	9.67	17.31	26.77	16.92	22.82	25.70	1.23	4.92
V.3	407.62	23.70	6.02	11.26	4.03	7.39	12.97	4.76	9.81	16.76	27.30	22.73	22.23	28.81	1.31	5.06
VI.1	383.06	20.79	5.94	11.30	3.98	7.07	13.41	4.72	9.37	17.62	25.82	13.71	23.17	24.62	1.17	4.86
VI.2	390.87	21.84	5.96	11.13	3.97	7.10	13.30	4.74	9.54	17.38	26.39	16.50	22.97	25.02	1.19	4.90
VI.3	401.47	23.16	5.97	11.02	4.01	7.20	13.22	4.74	9.72	16.95	27.00	22.14	22.41	27.80	1.24	5.02

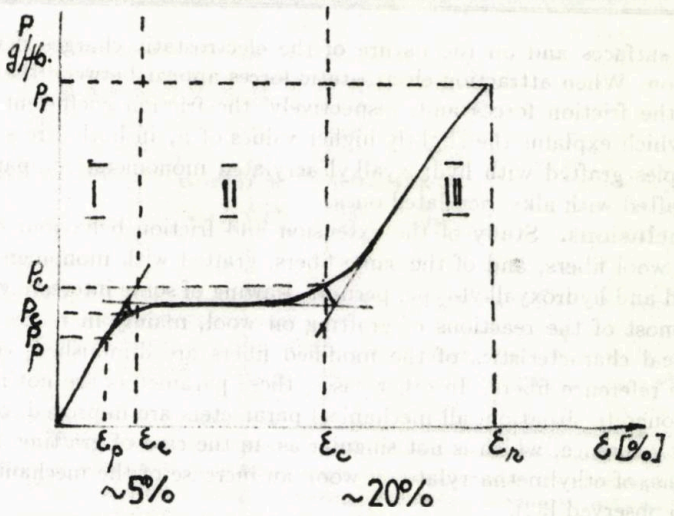

Fig. 2.– Schematic representation of the load-extension curve of wool fibre.

[30], according to whom two different regions, X and Y, are distinct. Through stretching, the X regions, having weaker links between microfibrils, start to permit, too, the transformation of α-keratin in its β form, a case in which a higher stretching load is necessary.

The results obtained from the mechanical properties suggest that fiber's architecture was not subjected to essential perturbations. As to the localization of the grafted polymer in the fiber's supramolecular structure, the results obtained will be discussed in subsequent studies.

Increase of the grafting degree induces decrease of the friction coefficients, both $\mu_{sf/m}$ and $\mu_{sf/f}$. Decrease in the values of the two coefficients are approximatively the same, more evident decreases (of about 50%) being recorded by the former, i.e. of 0.24 between the reference and the sample with the highest grafting degree; with the same samples, the latter decreases with 0.20 (which represents a 43% decrease comparatively with the reference).

Nature of the grafting monomer influences the μ_s values. In the case of hydrophylic monomers, with OH polar groups, (hydroxyalkyl acrylated monomers), the μ_s values are sensibly higher than of the hydrophobic, alkylacrylated ones, having no polar groups. Fibers' positioning during fiber/fiber friction is aleatory, some of them being stressed in the direction of scales' orientation, others in opposite direction. A comparison between the values obtained by us with those given in literature [2] (i.e., for friction in the scales' direction $\mu_{sf/f}$=0.13 and, in opposite direction, $\mu_{sf/f}$=0.61) leads to the conclusion that, during the experiments, most of the fibers have been placed in an aleatory manner, in scales of opposite sense.

The nature of fibers' friction force may be explained by the molecular-mechanical theory, according to which friction depends on both the mechanical action

between surfaces and on the nature of the electrostatic charges developed during friction. When attraction electrostatic forces appear between the fibers' polar groups, the friction forces and, respectively, the friction coefficient μ_s, also increase, which explains the slightly higher values of μ_s in both stress variants, for the samples grafted with hydroxyalkyl acrylated monomers, comparatively with those grafted with alkyl acrylated ones.

4. Conclusions. Study of the extension and friction behaviour of Romanian semifine wool fibers, and of the same fibers, grafted with monomers of the alkyl acrylated and hydroxyalkyl-type, permits drawing of some interesting conclusions.

In most of the reactions of grafting on wool, mainly in redox systems, the mechanical characteristics of the modified fibers are diminished, comparatively with the reference fibers. In other cases, these parameters are not modified [31]. In our concrete situation, all mechanical parameters are improved, comparatively with the reference, which is not singular as, in the case of grafting, induced by γ radiations, of ethylmethacrylate on wool, an increase of the mechanic parameters was also observed [32].

Table 2

Friction Behaviour of the Analized Fibers

No. of sample	Coefficient of fiber/metal static friction $\mu_{sf/m}$	Coefficient of fiber/fiber static friction $\mu_{sf/f}$
0	0.48	0.57
I.1	0.33	0.46
I.2	0.30	0.41
I.3	0.24	0.37
II.1	0.37	0.49
II.2	0.35	0.44
II.3	0.29	0.39
III.1	0.41	0.52
III.2	0.38	0.47
III.3	0.34	0.45
IV.1	0.39	0.50
IV.2	0.36	0.45
IV.3	0.32	0.41
V.1	0.42	0.53
V.2	0.41	0.51
V.3	0.36	0.48
VI.1	0.45	0.54
VI.2	0.44	0.52
VI.3	0.39	0.50

All these observations should be correlated with the mechanism of the grafting reactions and with the structural elements of the both nonmodified and modified

fiber, a problem to which further investigations should be devoted.

By comparing these results with previous determinations of physico-mechanical parameters for chemically non-modified wool fibers [33], a better uniformization (restriction of the domain of values) was observed, as induced by grafted copolymerization on wool, initiated with UV radiations, of alkyl and hydroxyalkyl acrylated monomers.

Also, a good correlation was found between the breaking parameters, determined on a Fafegraph dynamometer, with those previously calculated on a Digital Electronic Fiber Tester dynamometer [23],[24].

Also, grafting improved fibers' behaviour to friction, in parallel with decreasing the static friction coefficients, which influences favourably both pilling and fibers' filling.

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GREFAREA LÂNII PRIN INIŢIERE CU RADIAŢII UV
V. Caracterizarea prin metode mecanice a lânii grefate cu monomeri de tip alchil şi hidroxialchil acrilaţi

(Rezumat)

Se efectuează un studiu complet, din curbele forţă–alungire, privind comportarea mecanică a fibrelor de lână românească sort 22 grefate cu şase tipuri de monomeri. Se compară aceste valori cu cele obţinute pentru fibrele martor.

De asemenea, se urmăreşte comportarea fibrelor modificate şi nemodificate chimic la solicitări de frecare prin determinări ale coeficienţilor de frecare statică: fibră/metal şi fibră/fibră.

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Tomul XLI (XLV), Fasc. 3-4, 1995
Secţia VIII
TEXTILE. PIELĂRIE

STRUKTURVERÄNDERUNGEN DES AUF FLEIERN FÜR SPINNBÜSCHEL MIT UNKONVENTIONELLEN STRECKWERKEN BEARBEITETEN VORGARNS

VON
CARMEN CUZIC-ZVONARU

1. Einführung. In unserem Land sowie auch auf weltweiter Ebene entspricht der Fleier für das Spinnbüschel nicht mehr den Forderungen der aktuellen Technik [1],...,[4] und zwar wegen der am Streckwerk angewandten konstruktiven Lösung: er hat eine übertriebene Anzahl von Einzelteilen; verlangt hohe Genauigkeit beim Ausführen; der Geräuschpegel ist hoch; schwieriges Instandehalten; schwerfälliges Bedienen; hoher Leistungsverbrauch.

Wegen Begrenzung der Fallzahlen der Fangbüchsen auf nur 350/Min. variiert die Drehzahl der Spinnflügel zwischen 550...750 U/Min.

2. Experimenteller Teil. Die in der Halbkamm-Flachsspinnerei erzielte Erfahrung beim Einführen des Fleiers Schlumberger mit nadellosem Streckwerk beweist, daß die aktuelle Lösung auch in der gekämmten Flachsspinnerei neu bewertet werden muß[5],[6].

Bei den Versuchen wurden drei Arten von Streckwerken verwendet:

a) Streckwerk mit einfachem Nadelfeld (Bolelli), Abb.1 *a*;

b) Streckwerk mit doppelter Muffe (Schlumberger), Abb.1 *b*;

c) Streckwerk mit einfacher Muffe und schwimmenden Zylindern (SACM), Abb.1 *c*.

Bei den letzen zwei Varianten wurde der Klemmlinienabstand um 500 mm vergrössert, und zwar durch den Einbau eines zusätzlichen Speisungspaares.

Die Forschung verfolgte, vergleichend, folgende Aspekte:

– die Art der Fortsetzung des Individualisierungsprozesses der Fasern im Streckwerk des Fleiern;

– Gleichmässigkeit bezüglich Feinheit und Festigkeit der aus den drei Kategorien von Vorgarn hergestellten Fäden.

Im auf dem Fleier gespeisten Band hatten die Fasern Nm_f 309 und l_f = 189 mm. Die Abbildungen 2,...,4 synthetisieren die vorher aufgezählten Aspekte hinsichtlich der Dispersionsparameter und der Variation von:

– Länge und Feinheit der Fasern aus dem Vorgarn (*a*) und (*b*);

– Feinheit auf mittleren Abschnitten (1 m) der Vorgarne (*c*);

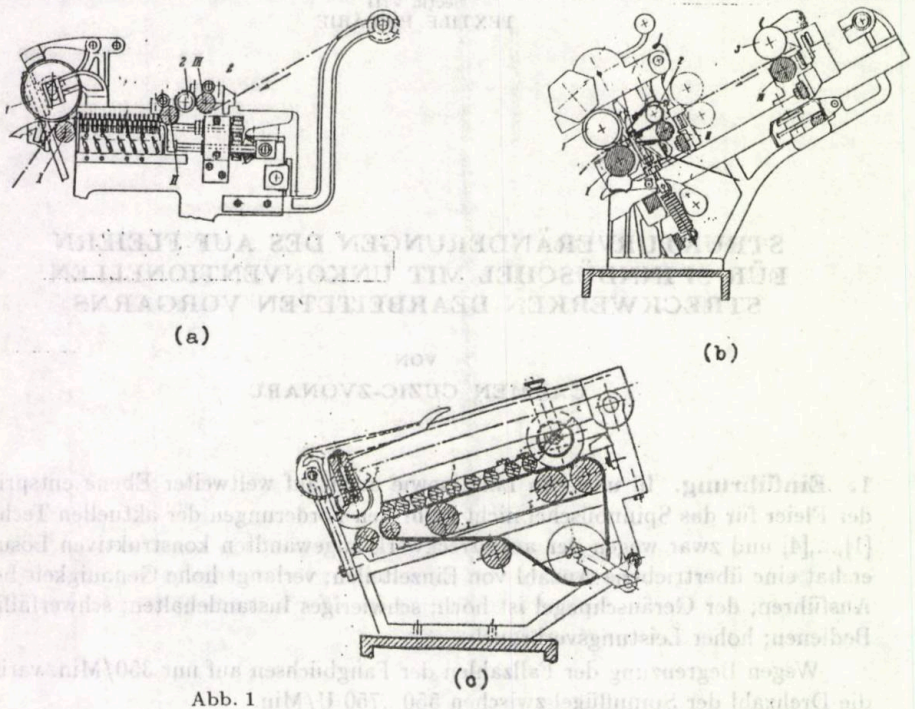

Abb. 1

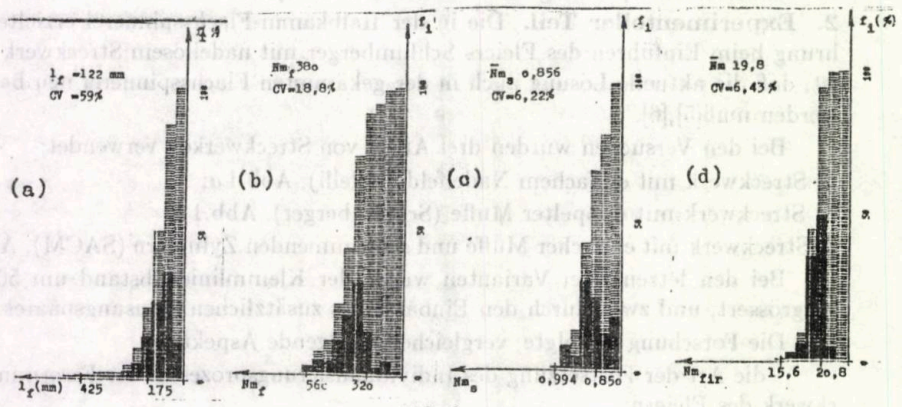

Abb. 2

– Feinheit der Fäden, hergestellt mit Nm 20, nass gesponnen (*d*).

Die Ergebnisse sind besonders wichtig für die Abteilung Flachs-Hanf. Folglich treten Probleme hervor, die sowohl von den Fachleuten für Maschinenbau, als auch von denjenigen für Flachsbearbeitung im Kammprozess beachtet werden müssen.

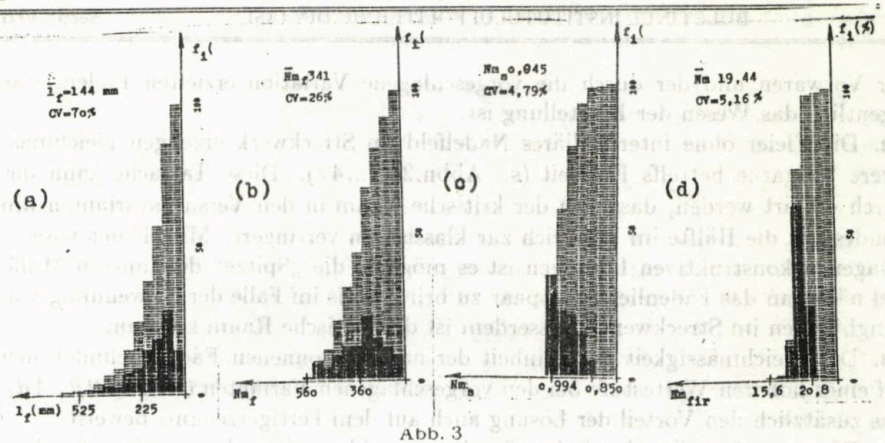

Abb. 3

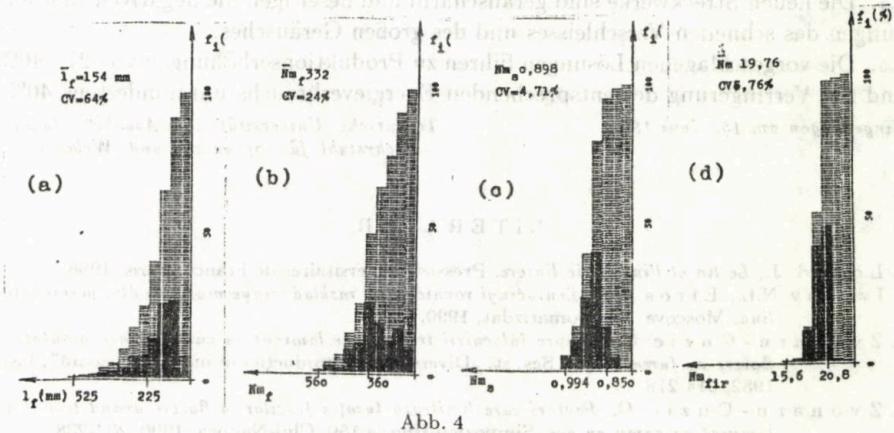

Abb. 4

3. Schlussfolgerungen

3.1. Im Streckwerk des Fleiers geht die Individualisierung der Fasern weiter, jedoch zwischen der klassischen Variante mit Feld und den beiden vorgeschlagenen Lösungen sind die Unterschiede unbedeutend. Die Erklärung ist eine rationelle. Es handelt sich um ein in die Endphase der Vorbereitung vor dem Spinnen gelangte Material, das einer progressiven Individualisierung schon unterworfen wurde, und zwar durch die Spinnvorbereitungsgeräte nach dem Durchgang durch 6...8 Nadelfelder mit Klemmlinienabständen von über 500 mm. Zieht man in Betracht, dass das Spinnen in nassem Zustand durchgeführt wird und ist die Gleichmässigkeit der Vorgarnfeinheit sowie auch die Parameter einer Immersion mit schnellerer Schwelldynamik der mittleren Lamelle gesichert, dann kann der Erfolg nicht mehr ausbleiben und es gibt keinen Grund mehr, das alte Streckwerk auf der Maschine zu behalten.

Die Unterschiede bezüglich Länge und Feinheit der technischen Fasern von einer Variante zur anderen sind unbedeutend im Vergleich zu einer höheren Qualität

der Vorwaren und der durch die vorgeschlagene Variation erzielten Fäden, was eigentlich das Wesen der Herstellung ist.

3.2. Die Fleier ohne intermediäres Nadelfeld im Streckwerk erzeugen gleichmässigere Vorgarne betreffs Feinheit (s. Abbn.2*c*, ..., 4*c*). Diese Tatsache kann dadurch erklärt werden, dass sich der kritische Raum in den Versuchsvarianten um mindestens die Hälfte im Vergleich zur klassischen verringert. Mittels der vorgeschlagenen konstruktiven Lösungen ist es möglich, die „Spitze" der inneren Muffe viel näher an das Fadenlieferungspaar zu bringen als im Falle der Anwendung von Fangbüchsen im Streckwerk. Ausserdem ist der kritische Raum konstant.

3.3. Die Gleichmässigkeit der Feinheit der nass gesponnenen Fäden befindet sich auf einer höheren Wertestufe bei den vorgeschlagenen Varianten (s.Abbn.2*d*...4*d*), was zusätzlich den Vorteil der Lösung auch auf dem Fertigerzeugnis beweist.

3.4. Die neuen Streckwerke sind geräuscharm und beseitigen die negativen Erscheinungen des schnellen Verschleisses und des großen Geräusches.

3.5. Die vorgeschlagenen Lösungen führen zu Produktionserhöhungen von 27...40% und zur Verringerung des entsprechenden Energieverbrauchs um mindestens 40%.

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MODIFICĂRI STRUCTURALE ALE SEMITORTULUI PRELUCRAT PE FLAIERE CU TRENURI DE LAMINAT NECONVENŢIONALE

(Rezumat)

Rezultatele deosebite obţinute în ţară şi în străinătate prin introducerea flaierului Schlumberger în filaturile semipieptănate de in au determinat cercetarea extinderii soluţiei şi la prelucrarea fuiorului, unde, în prezent, se folosesc în exclusivitate trenuri de laminat cu câmp de ace.

Se prezintă comparativ soluţia clasică (varianta Bolelli) cu două variante noi, neconvenţionale (variantele constructive Schlumberger şi SACM). Alimentând acelaşi material pe cele trei flaiere se fac interpretări privind intervenţia trenului de laminat asupra modificărilor de fineţe şi de lungime ale fibrelor din semitort şi asupra calităţii semitortului şi a firelor obţinute.

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Secţia VIII
TEXTILE. PIELĂRIE

NEUTRALISATOR DER ELEKTROSTATISCHEN AUFLADUNGEN

VON
GH. ANTONIU

1. Einleitung. Die Bedeutung der Beseitigung elektrostatischer Aufladungen in der textilien Industrie ist wohl bekant [1], [2]. Zu diesem Zweck werden häufig Ionisatoren mit Koronawirkung, die mit Gleichstrom, Wechselstrom, normaler Nezfrequenz, oder Hochfrequenz, gespeist werden, sowie radioaktiwe Ionisatoren eingesezt [3], [4].

Diese aber haben das Nachteil, dass der Ionisierungsstrom und dessen Polarität nicht kontrollierbar sind. Dass führt manchmal zur Unwirksamkeit dieser und kann sogar schädlich wirken.

Dieser Misstand ist darauf zurückzuführen, dass in der Textilindustrie, auf Grund der vielfachen Parameter von welchen die elektrostatische Aufladung der verarbeiteten Materialien abhängig ist, die Polarität sowie der Stand der am Material gespeicherten elektrostatischen Aufladungen voraussichtlich schwer zu bestimmen sind. (für das selbe Material, auf die selbe Maschine, kann manchmal eine positive, oder negative, oder überhaupt keine Aufladung festgestellt werden).

Dem zu Folge kann ein in betrieb gesezter Ionisator, manchmal zur Erhöhung der Aufladung am Material (anstat zur Verminderung) führen, oder zu einer efectiven Aufladung eines Materials.

Bei dem vom Autor vorgeschlagenen Neutralisator, wird dieser Misstand beseitigt, dadurch dass der Ionisator mit einer automaten Mess und Regelvorrichtung versehen ist, die den Ionisator nur dann wenn notwendig, und mit der entsprechenden Polarität in Betrieb setzt, wie in Abb. 1 vorgesehen, (Regel-schemata mittels eines milivoltmeters, bzw. durch elektronische Gleichstrom Relais. Abb. 2.

2. Neuttralisator mit Befehlsgeber durch Milivoltmeter Regelung. Abb. 1. Ein elektrometischer Messumformer (*1*) [5] erfasst die Polarität und den Stand der gespeicherten elektrostatischen Aufladung auf einem Material Band (*2*) und liefert am Ausgang eine Spannung (U) die proportionel mit der Aufladung einer gewissen Polarität ist. Diese Spannung wird einem Regelmilivoltmeter (*3*) mit „O" Mittelpunktscala zugeführt das, mittels zwei eigener Relais (*4,5*) die Inbetriebsetzung (Netzanschluss) einer der zwei Gleichstromionisatoren verschiedener Polarität (*6,7*), je nach Polarität des Materials steuert. Wenn dieses positiv geladen ist, trit

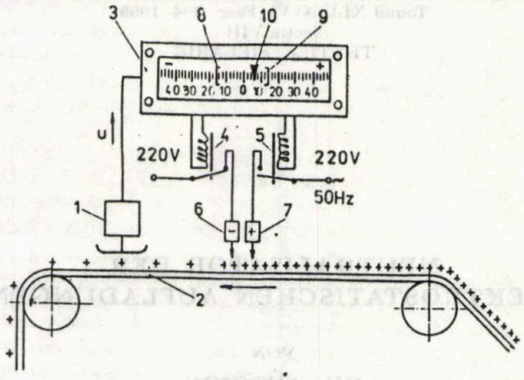

Abb. 1

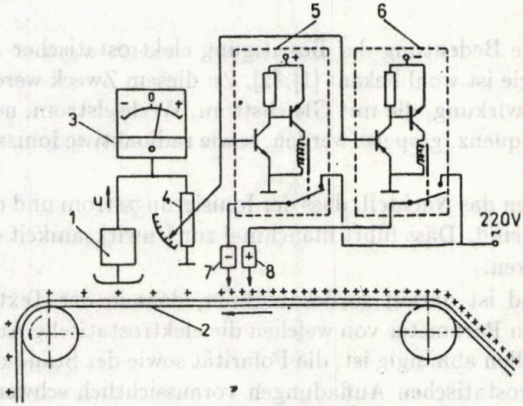

Abb. 2

der Ionisator mit negativer Elektronenabgabe in Betrieb (*6*), und umgekert.

Die nach der Neutralisierung akzeptierte Restaufladung des Matarials (es ist nicht notwendig und auch nicht wirtschaftlich komplet die elektrostatische Aufladung zu beseitigen, gleich welche Technologie angewendet wird) kan vom Operateuren vorgeschrieben werden (Sollwert) mittels 2 Index (*8,9*) die ausserhalb dieser Vorrichtung geregelt werden können.

Die 2 Index sind Bestandteil des Regelmilivoltmeters.

Die Anzeigerabweichung von „O" (links, rechts) des Milivoltmeters weist über den Stand des C/m^2 wie auch über die Polarität der Materialrestaufladung nach der Neutralisierung hin.

3. Gleichstrom relaisgesteuerter Neutralisator. Wie vorher angegeben, ein elektrometrischer Messumformer (*1*) liefert am Ausgang eine Spannung (U) die proportionäl mit einer elektrostatischen Materialband aufladung ist (*2*) und die gleiche Polarität gesitzt. Diese wird einem magnetelekrischen Voltmeter (*3*) mit „O" Mittelpunkt Scala das den Stand des C/m^2 wie auch die Polarität der Mate-

rialrestaufladung anzeigt u. gleichzeitig auch einem Potenziometer (*4*) zugeführt mit dem der Stand der akzeptierten Restaufladung des Materials vorgeschrieben (sollwert) werden kan.

Diese von (*4*) übernomene Spannung wird an zwei entgegengesezter Richtung transistorisierter Relais zugeführt (*5,6*) die, die Netzschaltung, einer der gleichrichtstrom Ionisatoren (*7,8*) je nach Polarität der elektrostatischen Aufladung die neutralisiert werden soll, Steuert.

Der vom Autor vorgeschlagener Neutralisator, hat den Vorteil das er zwecks Neutralisierung immer Ionen entsprechender Polarität liefert, und geht im Betrieb nur dann wen es notwendig ist, d.h. an der Grenze des akzeptierten C/m^2 Stand der Aufladung. Kann vom Operateur in Abhängigkeit der konkreten technologischen Bedürfnisen geregelt werden, dass einen rationällen Betrieb des Ionisators gewährleistet.

Im Vergleich mit dem in Abb. 1 beschriebenen Ionisator, hat der im Abb. 2 dem Vorteil dass er einfacher und biliger ist, aber bei diesem könen die akzeptierten Restaufladegrenzen (+) (−) nicht unabhängig vorgeschrieben werden (Sollwert).

Beide Varianten können mit im Land produzierten Materialien, Bestandteilen und Instrumente hergestellt werden.

4. Schlussfolgerungen. Aus dieser Beschreibung gehen folgende Schlussfolgerungen hervor:

1. Zwecks lokalen Neutralisierung der elektrostatischen Materialaufladungen im laufe ihrer Verarbeitung, werden Ionisatoren (neutralisatoren) verschidener Typen verwendet dessen Hauptmisstand darin besteht, das bei diesen der Ionnenfluss und Polarität unkontrolierbar sind.

2. Zwecks beseitigung dieser Misstände aktueler Ionisatoren, sieh Pkt.1, schlägt der Autor 2 Varianten von Aufladungsneutralisatoren origineler Lösung mit kontrolierbarer Polarität und Ionenfluss vor (Pkt.2 u.3), die mit Inlandkomponenten hergestelt werden können.

3. Der o.g. Neutralisator ist sowohl für die Textil-und Chemiefaserindustrie des Landes wie auch in anderen Industrien bei welchen die elekrostatischen Aufladungen im technologischen Prozes störend wirken anwendbar.

Eingegangen am 15. Dezember 1994

Technische Universität „Gh.Asachi", Jassy, Lehrstuhl für Spinnerei und Weberei

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NEUTRALIZATOR DE SARCINĂ ELECTROSTATICĂ

(Rezumat)

Se prezintă un neutralizator de sarcini electrostatice la care ionizatorul este asociat cu un dispozitiv de măsurare-reglare automată, în două variante, care pune în funcţiune ionizatorul numai atunci când este nevoie şi cu polaritatea necesară.

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Secţia VIII
TEXTILE. PIELĂRIE

SUR LA DISTRIBUTION DES FIBRES DANS LA SECTION TRANSVERSALE DES FILS ET SUR L'INFLUENCE DE CELLE-CI SUR LES PROPRIÉTÉS PRINCIPALES DES FILS

PAR
DEMETRA L. BORDEIANU et M. CIOCOIU

1. Introduction. Réaliser des fils à partir d'un mélange de coton et de fibres chimiques a suscité un intérêt spécial dès la production des métiers à filer à rotor. Bien que l'obtention des fils à partir de fibres synthétiques à 100% réprésente à peine 15% de la capacité mondiale de filage à rotor [1], l'usinage des mélanges, et surtout de ceux composés de coton et de polyester, est devenu chose courante. Les propriétés des fibres de coton et des fibres de polyester se complètent réciproquement et contribuent à la production de produits résistants et attractifs.

Etant donné que la résistance des fils à la traction est influencée surtout par les fibres qui sont placées au centre du fil, tandis que l'aspect des produits (éclat, chiffonnement, etc.) – par les fibres qui se trouvent à l'extérieur, la position des fibres dans les fils fabriqués à partir de mélanges a été l'objet de nombreuses recherches [1],...,[4].

2. Expérimentations propres. En partant de l'idée que les différences entre les propriétés des fils filés sur des métiers à filer à rotor et les propriétés des fils filés sur des métiers à filer à anneaux sont dues aussi aux différences concernant la distribution des fibres dans la section transversale des fils, on a analysé des fils Nm 40 obtenus par le procedé classique et non-conventionnel à rotor, à partir du mélange de coton et de fibres de polyester. On a réalisé les mélanges en modifiant le rapport entre le nombre des rubans de coton et de polyester alimentées au premier passage de laminoire.

Les caractéristiques principales des fibres de coton et des fibres de polyester sont présentées aux Tableaux 1 et 2.

La distribution des fibres en section transversale des fils a été appréciée par l'indice de migration calculé selon la méthode Hamilton [2]; les valeurs obtenues figurent au Tableau 3.

Il est à remarquer les valeurs absolues des indices de migration moins importants pour les fils obtenus dans le système non-conventionnel, ce qui démontre que la distribution des fibres est plus uniforme dans la section des fils, la migration des fibres étant mois accentuée que pour les fibres classiques.

Tableau 1

Caractéristiques des fibres de coton

La caractéristique	U.M.	Soviétique moyen 2
Densité de longueur	mtex(Nm)	182(5477)
Indice micronnaire		3,72
Longueur Stappel	mm	29,5
Résistance Pressley	lbs/inch	80,967
Coefficient de maturité (mercérisation)	%	86
Impuretés	%	2,89
Contenu en fibres courtes:		
– en-dessous de 14 mm	%	29,0
– en-dessous de 10,5 mm	%	18,7

Tableau 2

Caractéristiques principales des fibres de polyester

La caractéristique	U.M.	Fibres polyester
Densité de longueur	dtex(den)	1,67(1,51)
	Cv %	5,12
Longueur moyenne	mm	37,88
	Cv %	4,52
Charge à la rupture	cN/fibre	7,26
	Cv %	19,56
Tenacité	cN/dtex	4,34
Défauts des fibres:		
– fibres collées	%	0.0039
– fibres non-étirées	nr./100 g	20,96
– fibres courbées	nr./100 g	2,04

Tableau 3

Valeurs des indices de migration. Méthode Hamilton

Variante PES/Coton (%)	Classique		OE	
	Polyester	Coton	Polyester	Coton
33/67	–11,39	11,39	–3,779	3,779
50/50	–13,683	13,68	–9,42	9,42
67/33	–11,737	11,73	–7,417	7,467

On présente au Tableau 4 les caractéristiques principales des fils réalisés.

Il faut remarquer l'allongement à la rupture, qui est plus important pour les fils OE. L'augmentation de la quantité de fibres polyester du mélange détermine une croissance plus accentuée (73,58% pour le fil OE par rapport à 64% pour le fil classique) de l'allongement des fils non-conventionnels. Pour ce système de filage, l'allongement des fils est donc influencé surtout par l'allogement des fibres.

L'uniformité Uster des fils OE est plus réduite que celle des fils classiques,

Tableau 4

Caractéristiques principales des fils Nm 40

Mélange PES/Coton (%)	Nm	Cv Nm (%)	Resistance (cN/tex)	Cv Uster (%)	Faibles/ 1000 m	Grosseurs/ 1000 m	Neps/ 1000 m
Fil open end							
0/100	39,23	3,01	9,46	11,48	17,00	40,0	116
17/83	39,18	2,93	9,17	12,3	22,4	24,0	51
33/67	40,48	3,82	9,24	11,72	27,00	76,0	106
50/50	39,93	2,09	10,03	12,46	26,7	67,2	96
67/33	39,65	2,73	11,41	12,76	36,8	64,0	52
100/0	40,7	3,13	15,15	13,18	46,4	86,4	92
Fil conventionnel							
0/100	39,81	4,11	12,16	15,02	426,0	1615,0	873
17/83	39,73	4,37	11,92	15,13	372,0	876,0	1123
33/67	40,08	2,24	12,35	14,96	348,0	1812,8	1488
50/50	39,10	5,04	13,4	15,98	576,0	536,0	414
67/33	40,18	3,95	16,51	15,32	110,4	966,4	940
100/0	40,2	4,13	25,02	15,72	326,2	1215,4	1011

de 16,15% jusqu'à 23,57%. Pour le système de filage OE, elle s'accentue avec l'augmentation du pourcentage de fibres de polyester, pendant que pour le système de filage classique, elle reste presque constante.

Les diagrammes présentés en Fig.1 concernant les taux de participation à la tenacité des fils nous mènent aux conclusions suivantes:

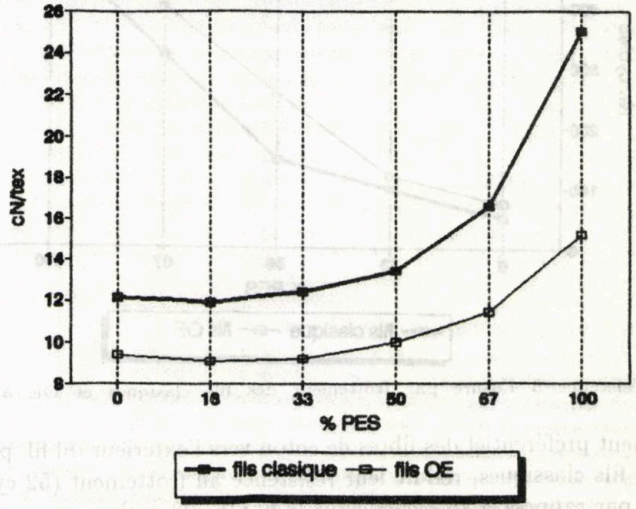

Fig. 1.– Tenacité des fils en fonction du taux de participation des fibres en mélange.

– les fils obtenus en filature open-end ont une tenacité moindre que les fils obtenus en filature conventionnelle à cause de la structure différente des deux types de fils, à cause du degré plus réduit d'orientation des fibres, mais aussi à cause

d'une distribution plus uniforme des fibres dans la section du fil. Le placement préférentiel des fibres polyester vers l'intérieur du fil, plus accentuée encore pour les fils classiques, contribue certainement à accentuer les différences entre les tenacités des deux types de fils, puisqu'on sait bien que les fibres du centre du fil sont celles qui influent décisivement sur cette caractéristique.

– le fait que la résistance des fibres est réflectée par la résistance des fils est incontestable, mais l'utilisation d'une petite proportion de fibres polyester peut réduire même la tenacité des fils (9,17 cN/tex pour le fil à 17% polyester et 9,24 cN/tex pour le fil à 33% polyester par rapport à 9,46 cN/tex pour le fil en 100% coton filé OE).

Une quantité qui dépasse 50% polyester a un effect benefique sur la tenacité des fils.

– les différences concernant les tenacités des fils obtenues par les deux systèmes de filage s'accentuent avec l'augmentation du pourcentage en fibres de polyester.

Bien que la tenacité des fils OE soit moindre, ils ont une meilleure résistance à l'usure par frottement (Fig.2).

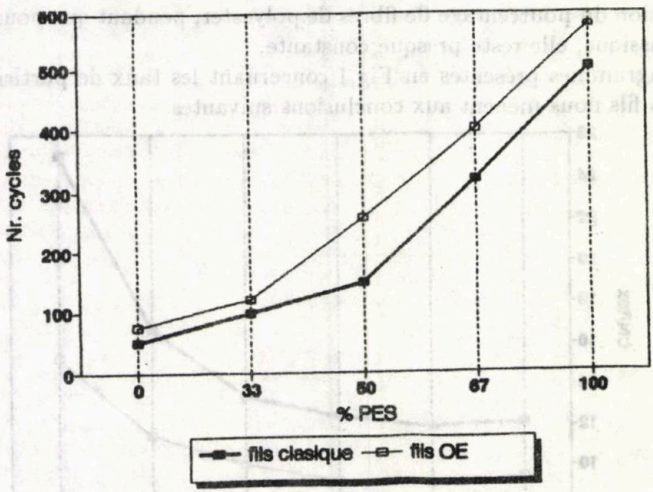

Fig. 2.– Résistence à l'usure par frottement des fils clasiques et OE à rotor.

Le placement préférentiel des fibres de coton vers l'extérieur du fil, plus accentué au cas des fils classiques, réduit leur résistence au frottement (52 cycles pour le fil classique par rapport à 76 cycles pour le fil OE; 98 cycles par rapport à 120 cycles; 148 cycles par rapport à 256 et – respectivement – 502 cycles par rapport à 574).

Les taux de participation des fibres en polyester influent à peu près dans la même mesure sur la résistance aux sollicitations d'usure des fils (les courbes sont à peu près parallèles).

3. Conclusions. La manière différente de formation des fils OE par rapport aux fils classiques apporte des différences entre les caractéristiques structurales et entre les propriétés des deux types de fils.

Les résultats obtenus par les fils analysés mettent en évidence les aspects suivants:

– pour les deux types de fils (classique et OE à rotor) on constate que les fibres de polyester se sont placées vers les zones extérieures.

– la migration des fibres dans les fils filés à rotor est moins accentuée par rapport à celle des fils classiques, influant sur les différences qui paraissent entre les tenacités des deux types de fils et sur leur résistance à l'usure.

– puisque les fils ont été réalisés à partir de la ,ê,e matière première, les valeurs plus réduites de la non-uniformité Uster des fils OE montrent que la non-uniformité par le système de filage classique est plus grande que celle qui est provoquée par la système de filage non-conventionnel.

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Université Technique „Gh.Asachi", Jassy,
Chaire de Filature et Tissage

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CU PRIVIRE LA DISTRIBUŢIA FIBRELOR ÎN SECŢIUNEA TRANSVERSALĂ A FIRELOR ŞI INFLUENŢA ACESTEIA ASUPRA PRINCIPALELOR PROPRIETĂŢI ALE FIRELOR

(Rezumat)

Se prezintă aspecte privind distribuţia fibrelor în secţiunea transversală a firelor Nm 40 apreciată prin indicele de migrare calculat după metoda Hamilton şi influenţa sa asupra principalelor caracteristici ale firelor clasice şi neconvenţionale cu rotor filate din diferite amestecuri de bumbac şi fibre poliesterice.

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TEXTILE. PIELĂRIE

RESEARCHES FOR INCREASING THE FINENESS OF FIBERS EXTRACTED FROM UNRETTED FLAX STEMS BY CHEMICAL PROCEDURES

BY
ADRIANA MUSTAŢĂ

1. Introduction. Ample investigations performed in recent years [1],...,[3] have led to the conclusion that, ever since the beginning of the flax spinning preparation, an essential requirement referred to the fineness of the flax fiber to permit its adaptation to the modern technologies applied at present in the processing of wool or cotton.

The techniques of stems processing and fiber extraction without retting followed by fiber bleaching, meet best the requirements induced by the new directions of evolution in flax industries [1],...,[4].

Several studies [5],...,[10] have been devoted to the process of unretted flax bleaching and to its further processing.

2. Experimental. The experiments discussed in the present paper aimed at determining the working parameters of the bleaching processes with sodium hypochlorite and hydrogen peroxide, applied to unretted flax fibers in order to increase their degree of fineness, as well as to equalize the effects of retting applied on flax stems. For a better experimental simulation of the conditions met in the sections of flax finishing, the concurrent influence exercised on the fibers was followed simultaneously, by varying some working parameters. Thus, unretted flax fibers produced by the C-460-L_2 card, containing 4% impurities and having a ponderated average length of 120 mm – the ponderation factor considered being the weight fibers – were bleached. The fibers were extracted from the Here-type stems, cultivated in the Joseni region.

The average fineness of the tested fibers was of Nm 150 (6.6 tex). Codification of the independent variables and selection of their variation interval are given in Table 1.

Programming of the experiments gave 31 variants, presented in Table 2.

The stages considered for each variant were: bleaching with sodium hypochlorite, at cold, followed by washing with cold water, then bleaching with 35% hydrogen peroxide and again washing with water 50°C, followed by rinsing with cold water, the duration of each washing being 10 minutes. Fineness of the bleached flax fibers, obtained in each variant, was determined by the standardized gravimetric method.

Table 1
Codification of the Independent Variables and Selection of their Variation Interval

No.	Independent variable	The level of variables				
		−2	−1	0	1	2
1.	e – concentration of bleaching solution with 35% hydrogen peroxide, [mL/L]	60	75	90	105	120
2.	g – temperature of bleaching solution with 35% H_2O_2, [°C]	20	37	54	72	90
3.	f – concentration of bleaching solution with sodium hypochlorite, [g/L active chlorine]	0.4	0.8	1.2	1.6	2.0
4.	h – total duration of the bleaching reaction, [hours]	1	2	3	4	5

3. Results and Discussion. Processing of the experimental data centralized in Table 2 led to a mathematical model of the fineness of unretted flax fibers, supplied by the card and bleached in 31 variants, of the following form:

$$y = 200 + 2e + 16f + 11.6g + 11.75h - 1.25e^2 + f^2 - 6.3g^2 + 3.625h^2 + \\ + 13.625ef + 11.5eg + 3.875eh - 2.3fg + 24.675fh + 1.89gh. \quad (1)$$

The regression equation (1) expresses adequately the phenomenon under study, as the difference between the measured and the calculated values on the fineness of unretted flax bleached fibers is lower than 10% (see Table 2).

Analysis of the graph plotted in Fig.1, evidencing the dependence between the fineness of the bleached fibers and the concentrations of the two bleaching agents, namely H_2O_2 and NaOCl, leads to the following conclusion: when the temperature of the bleaching solution with H_2O_2 (g) is 54°C and the total duration of the bleaching reaction (h) is 3 hours, the actions of the two oxidants occurring within equal time intervals (1.5 h – duration of the treatment with a NaOCl solution and 1.5 h – of that with a hydrogen peroxide solution, respectively), the greatest influence upon the fineness of unretted flax fibers is exerted by the concentration of the bleaching solution with sodium hypochlorite, f.

As to the influence of the concentration of sodium hypochlorite, f, and of the temperature of the bleaching solution with hydrogen peroxide, g, on the fineness of unretted flax fibers (Fig.2), the observation to be made is that – out of the two independent parameters considered – a greater impact is exercised by the concentration of the bleaching solution with hypochlorite, f, as its lower variations induce shifting of the fineness of unretted flax fibers, from one level curve to another.

Referring to the influence of the sodium hypochlorite concentration, f, and of the duration of the bleaching reaction, h, on the degree of unretted flax fineness (Fig.3), a higher influence is exercised by the latter parameter, h.

Table 2

Experimental Programme for Increasing the Fineness of Fibers Extracted from Unretted Flax Stems by Chemical Procedures

Number of experiment	e_{cod}	f_{cod}	g_{cod}	h_{cod}	e	f	g	h	$\overline{Nm}_{fibres}$	
									y measured	y estimated
1	-1	-1	-1	-1	75	0.8	37	2	226	230.6
2	1	-1	-1	-1	105	0.8	37	2	170	172.0
3	-1	1	-1	-1	75	1.6	37	2	188	186.0
4	1	1	-1	-1	105	1.6	37	2	186.5	186.5
5	-1	-1	1	-1	75	0.8	72	2	195	193.0
6	1	-1	1	-1	105	0.8	72	2	183	185.0
7	-1	1	1	-1	75	1.6	72	2	154	143.8
8	1	1	1	-1	105	1.6	72	2	207	190.3
9	-1	-1	-1	1	75	0.8	37	4	172	154.6
10	1	-1	-1	1	105	0.8	37	4	135.1	116.1
11	-1	1	-1	1	75	1.6	37	4	194	213.3
12	1	1	-1	1	105	1.6	37	4	230	229.3
13	-1	-1	1	1	75	0.8	72	4	179	197.2
14	1	-1	1	1	105	0.8	72	4	222	204.7
15	-1	1	1	1	75	1.6	72	4	236	246.7
16	1	1	1	1	105	1.6	72	4	308.7	308.7
17	-2	0	0	0	60	1.2	54	3	191	195.5
18	2	0	0	0	120	1.2	54	3	199	199.0
19	0	-2	0	0	90	0.4	54	3	181	172.0
20	0	2	0	0	90	2.0	54	3	229	236.0
21	0	0	-2	0	90	1.2	20	3	148.7	151.6
22	0	0	2	0	90	1.2	90	3	202.5	198.0
23	0	0	0	-2	90	1.2	54	1	191	191
24	0	0	0	2	90	1.2	54	5	238	238
25	0	0	0	0	90	1.2	54	3	179	200
26	0	0	0	0	90	1.2	54	3	220	200
27	0	0	0	0	90	1.2	54	3	195.5	200
28	0	0	0	0	90	1.2	54	3	185	200
29	0	0	0	0	90	1.2	54	3	197	200
30	0	0	0	0	90	1.2	54	3	195	200
31	0	0	0	0	90	1.2	54	3	219	200

Obs.: y is the fineness of fibers; e, f, g, h are defined in Table 1.

Between the temperature of the bleaching solution with hydrogen peroxide, g, and the total duration of the oxidation reaction, h a relation of interdependence occurs, each of the two parameters influencing the other one's action (Fig.4). Within the experimental domain there may be observed the constant level curves corresponding to the fineness of fibers – Nm 175, Nm 200 and Nm 250. An economically advantageous variant is that in which a fiber fineness of Nm 250 is obtained, under the following conditions: concentration of the bleaching solution with 35% hydrogen peroxide – 60 mL/L, concentration of the sodium hypochlorite solution – 1.1

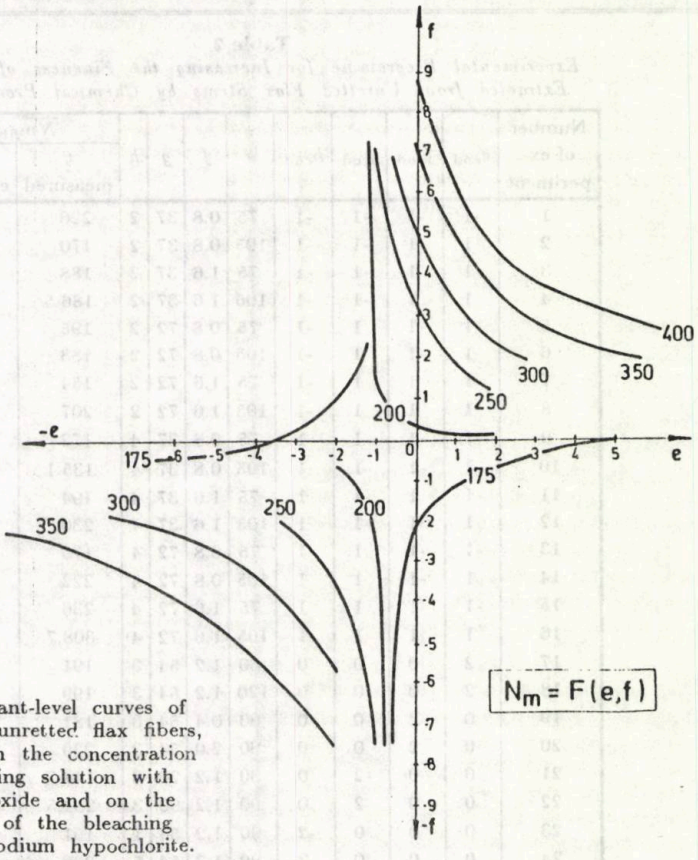

Fig. 1.– Constant-level curves of the fineness of unretted flax fibers, as depending on the concentration of the bleaching solution with hydrogen peroxide and on the concentration of the bleaching solution with sodium hypochlorite.

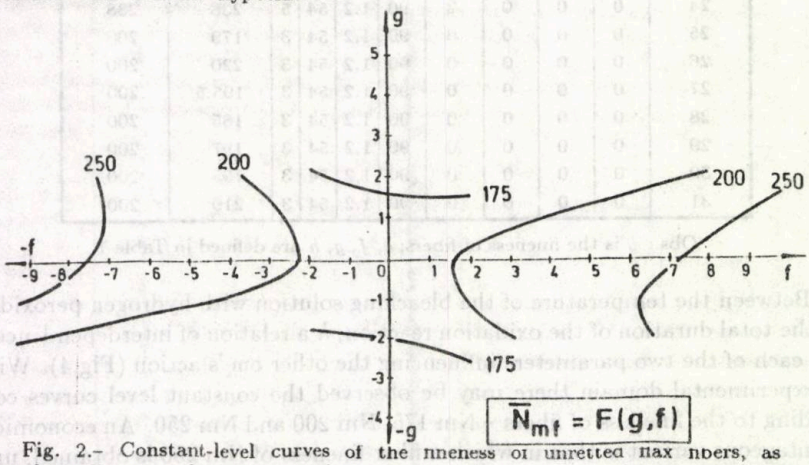

Fig. 2.– Constant-level curves of the fineness of unretted flax fibers, as depending on the concentration of the sodium hypochlorite, f, and on the temperature of the bleaching solution with hydrogen peroxide, g.

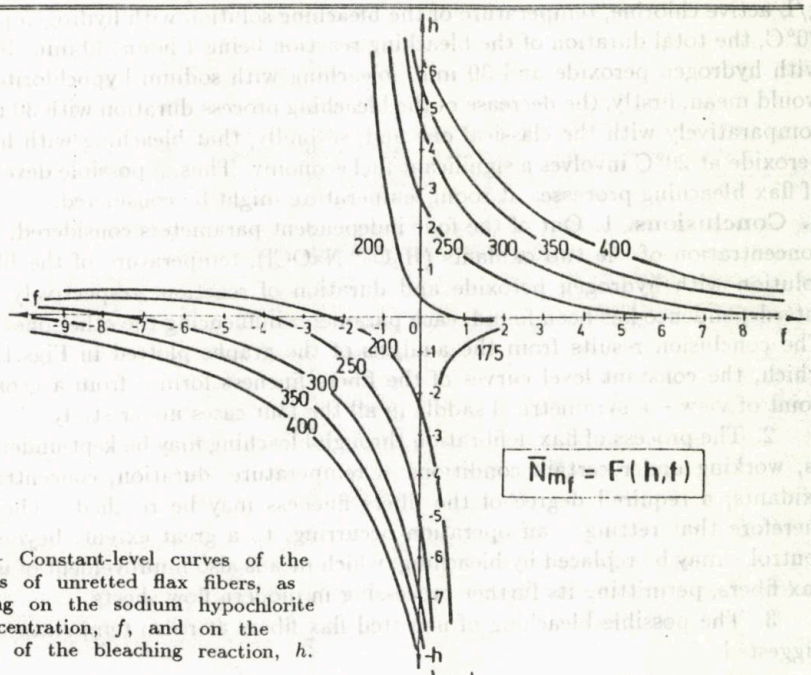

Fig. 3.– Constant-level curves of the fineness of unretted flax fibers, as depending on the sodium hypochlorite concentration, f, and on the duration of the bleaching reaction, h.

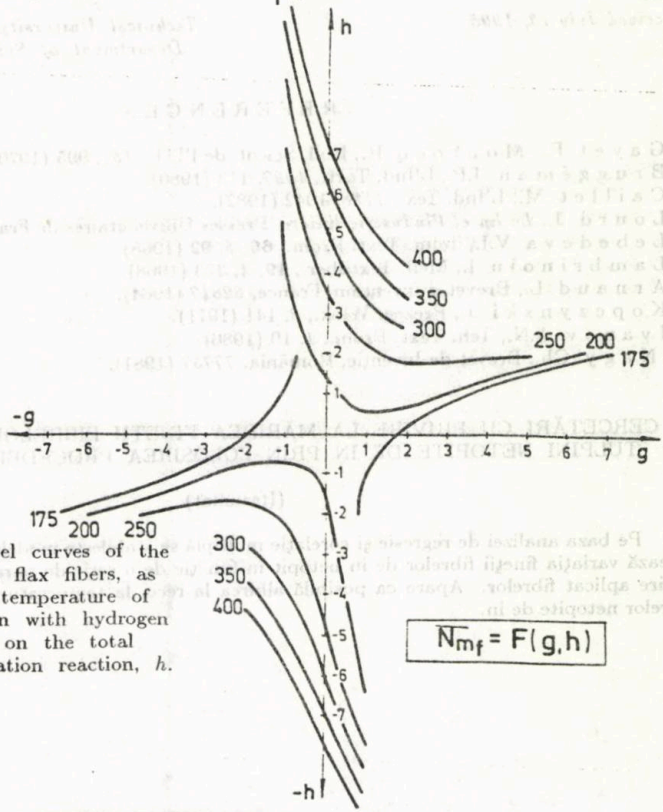

Fig. 4.– Constant-level curves of the fineness of unretted flax fibers, as depending on the temperature of the bleaching solution with hydrogen peroxide, g, and on the total duration of the oxidation reaction, h.

g/L active chlorine, temperature of the bleaching solution with hydrogen peroxide: 20°C, the total duration of the bleaching reaction being 1 hour (30 min. bleaching with hydrogen peroxide and 30 min. bleaching with sodium hypochlorite). This would mean, firstly, the decrease of the bleaching process duration with 30 minutes, comparatively with the classical one and, secondly, that bleaching with hydrogen peroxide at 20°C involves a significant fuel economy. Thus, a possible development of flax bleaching processes at room temperature might be considered.

4. Conclusions. 1. Out of the four independent parameters considered, namely: concentration of the two oxidants (H_2O_2; NaOCl), temperature of the bleaching solution with hydrogen peroxide and duration of reaction, respectively, a close interdependence has been found, each parameter influencing the other ones' action. The conclusion results from the analysis of the graphs plotted in Figs.1,...,4, in which, the constant level curves of the fibers fineness form – from a geometrical point of view – a symmetrical saddle in all the four cases under study.

2. The process of flax defibration through bleaching may be kept under control as, working under certain conditions of temperature, duration, concentration of oxidants, a required degree of the fibers fineness may be reached. The idea is therefore that retting – an operation occurring, to a great extent, beyond one's control – may be replaced by bleaching, which means also improvement of unretted flax fibers, permitting its further processing in modern flow sheets.

3. The possible bleaching of unretted flax fibers at room temperature is also suggested.

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CERCETĂRI CU PRIVIRE LA MĂRIREA FINEŢII FIBRELOR EXTRASE DIN TULPINI NETOPITE DE IN PRIN FOLOSIREA PROCEDEELOR CHIMICE

(Rezumat)

Pe baza analizei de regresie şi corelaţie multiplă se stabileşte modelul matematic ce aproximează variaţia fineţii fibrelor de in netopit în funcţie de o serie de parametri ai procesului de albire aplicat fibrelor. Apare ca posibilă albirea la rece, la temperatura mediului ambiant, a fibrelor netopite de in.

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ALGORITHM FOR THE CALCULATION OF THE COMPACTNESS DEGREE FOR DOUBLE WOVENS

I. THE COMPACTNESS DEGREE FOR DOUBLE WOVENS WITH ASCENDING STITCHING

BY

DANIEL CHINCIU, GABRIEL CORNELIU CHINCIU and IRINA CRISTIAN

1. Introduction Double wovens are formed of at last four systems of yarns, namely: a system of superior warp (US), a system of inferior warp (UI), one of superior weft (BS) and one of inferior weft (BI), respectively. They form two simple, distinct and superposed wovens, each of them containing a yarn system of warp and one of weft yarns, respectively.

The unique, double woven may be obtained through interlacing weave of the simple woven materials.

Stitching may be performed by the following methods:

a. *stitching with their own yarns* of the simple wovens, in one of the following three variants:

a.1. *ascending-type interlacing weave*, characterized by the fact that the inferior warp is lifted and linked over the superior weft;

a.2. *descending-type interlacing weave*, characterized by the fact that the superior warp is moved downwards and linked behind the inferior weft;

a.3. *mixed interlacing weave*, characterized by the concurrent utilization of the two types of stitching: ascending and descending. The latter one is applied when a stronger interlacing weave of the two woven materials is required.

b. *stitching with additional* yarns, which is achieved in practice in two variants:

b.1. *interlacing weave* with stitching warp yarns (UIs)

b.2. *interlacing weave* with stitching weft yarns (BIs).

Mixed stitching with special yarns is not applied in practice, as on one hand, they complicate the technology of fabrication and, on the other, stitching with only one system assure sufficient fastness of the interlacing weave operation.

Interlacing weave with yarns of one's own shows technological advantages, as employing less systems of yarns for the woven's formation; at the same time, disadvantages – evidenced by an inequal stress of the systems of yarns – are present.

Stitching with special yarns complicate the fabrication technology, without inducing significantly different stresses between the yarn systems forming the two

wovens.

This latter aspect is less evident for stitching with a warp system, and more pronunced when employing stitching with a weft system capable – in the case of some unsuitable interlacing weave for the woven's face – of influencing negatively its surface appearance.

The compactness degree for double wovens, to which stitching is made either with the layers' own yarns or with special, weft or warp yarns, is calculated for each system of yarns belonging to the woven with the following relations:

$$Ku_x = \frac{Pu_x \cdot L_{Ru_x}}{Ru_x}, \tag{1}$$

$$Kb_y = \frac{Pb_y \cdot L_{Rb_y}}{Rb_y}, \tag{2}$$

where x and y represent the system of warp and, respectively, of weft, belonging to the double woven.

The compactness degree of the double wovens is calculated by summing up the degrees of compactness on yarn systems with the relations:

$$Kt = \frac{\sum_{x=1}^{m} Ku_x + \sum_{y=1}^{n} Kb_y}{m+n}, \tag{3}$$

where m is the number of warp systems in the structure of the double woven; n – number of weft systems in the same woven.

2. Calculation of the compactness degree for a double woven, alternance ratio 1:1, identical faces, ascending stitching (LD - IA). The block diagram of the interlacing weave , partial drawing and the general drawing of the link are plotted graphically in Figs. 1 and 2.

3. Calculation of the compactness degree for the warp system. The compactness degree, Ku_x, of each warp system is calculated with relation (1), in which the length of the warp ratio, L_{Ru_x}, for the two systems of warp, at maximum technological thickness, is calculated as plotted in Fig.3, with the following relations:

– the length of ratio in the warp of the superior warp is:

$$L_{Ru_s} = R_{u_s} \cdot d_{u_s} + x_{b_s} \cdot t_{b_s}, \tag{4}$$

$$L_{Ru_i} = Ru_i \cdot d_{u_i} + x_{b_i} \cdot t_{b_i} + x_{b_{is}} \cdot t_{b_{is}}, \tag{5}$$

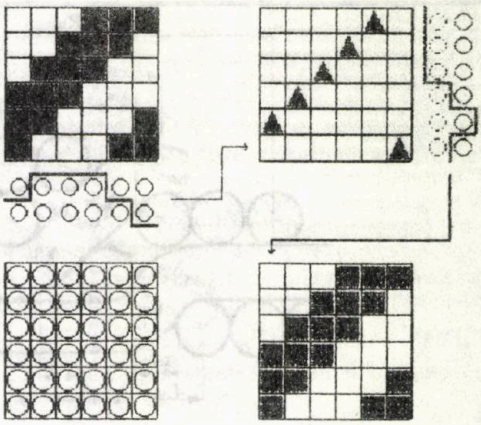
where:

$$x_{b_s} = Lu_s - d_{u_s}, \tag{6}$$

$$x_{b_i} = Lu_i - d_{u_i}, \tag{7}$$

$$x_{b_{is}} = Lu_{is} - d_{u_i}, \tag{8}$$

while:



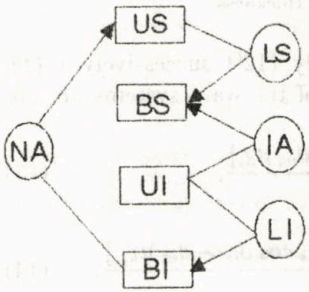


Fig. 1.– The block diagram of the double interlacing weave with ascending stitching.

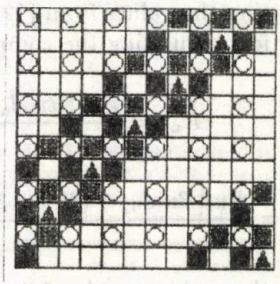


Fig. 2.– Double woven, ascending stitching alternance ratio 1US:1UI.

$$Lu_s = (du_s + db_s)\cos\beta_s = D_s \cdot \cos\beta_s, \tag{9}$$

$$Lu_i = (du_i + db_i)\cos\beta_i = D_i \cdot \cos\beta_i, \tag{10}$$

$$Lu_{is} = (du_i + db_s)\cos\beta_{is} = D_{is} \cdot \cos\beta_{is}. \tag{11}$$

Replacing (9) in (6) and the result in (4), the following relation is obtained:

$$L_{Ru_s} = Ru_s \cdot du_s + (Ds \cdot \cos\beta_s - du_s)tb_s. \tag{12}$$

Further on, by replacing (10) in (7) and (11) in (8) and the obtained result in (5), one gets the relation:

$$L_{Ru_i} = Ru_i \cdot du_i + (D_i \cdot \cos\beta_i - du_i)tb_i + (D_{is} \cdot \cos\beta_{is} - du_i)tb_{is}. \tag{12'}$$

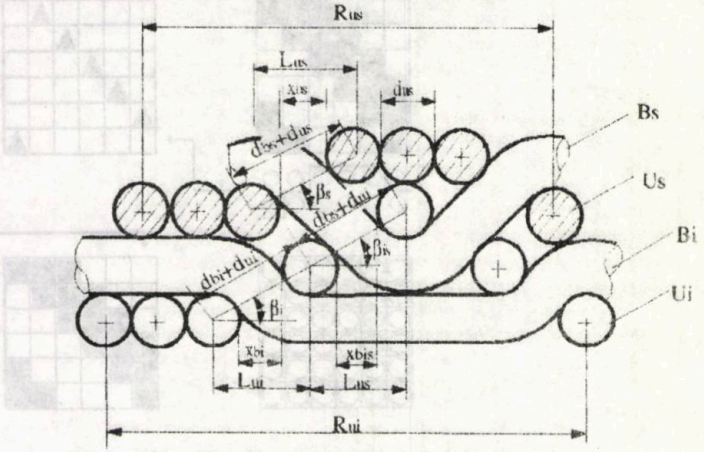


Fig. 3.- Double woven, ascending stitching, cross section. Maximum technological thickness.

On replacing the values from (12) and, respectively, (12′), successively in (1), the relations for calculating the compactness degree of the warp systems are obtained:

$$K_{u_s} = \frac{Pu_s[Ru_s d_{u_s} + (D_s \cos\beta_s - d_{u_s})t_{b_s}]}{Ru_s}, \tag{13}$$

$$K_{u_i} = \frac{Pu_i[Ru_i d_{u_i} + (D_i \cos\beta_i - d_{u_i})t_{b_i} + (D_{is} \cos\beta_{is} - d_{u_i})t_{b_{is}}]}{Ru_i}, \tag{14}$$

where: β_{is} is the curbing angle of the inferior warp, due to interlacing weave with the superior warp; β_s – curbing angle of the superior warp, due to interlacing weave with the superior warp; β_i – curbing angle of the inferior warp, due to interlacing weave with the inferior warp; tb_s – number of passings of the superior warp yarns through the yarns of the superior warp within a ratio; tb_i – number of passings of the inferior warp yarns through the yarns of the inferior warp within a ratio; tb_{is} – number of passings of the superior warp yarns through the yarns of the inferior warp within a ratio; xb_{is} – distance between the in plane projection of the cross centers of two consecutive yarns of inferior warp through which a yarn of superior warp is passed; xb_i, xb_s – distance between the in plane projection of the cross centers of two consecutive yarns of inferior warp through which a yarn of inferior warp is passed ,inferior warp and respectively superior warp; Lu_s, Lu_i, Lu_{is} – distance between the in plane projection of the cross centers of two consecutive yarns of warp through which a weft yarn (geometrical thickness – in mm) is passed.

4. Calculation of the degree of compactness for weft systems. Length of the weft ratio for the two systems of weft, at a maximum technological thickness is calculated as presented in Fig.4, by means of the following relations:

$$L_{Rb_s} = R_{b_s} \cdot d_{b_s} + x_{u_s} \cdot t_{u_s} + x_{u_{is}} \cdot t_{u_{is}}, \tag{15}$$

$$L_{R_{b_i}} = R_{b_i} \cdot d_{b_i} + x_{u_i} \cdot t_{u_i}, \tag{16}$$

where:

$$x_{u_s} = (d_{u_s} + d_{b_s}) \cdot \cos\alpha_s - d_{b_s} = D_s \cdot \cos\alpha_s - d_{b_s}, \tag{17}$$

$$x_{u_i} = (d_{u_i} + d_{b_i}) \cdot \cos\alpha_i - d_{b_i} = D_i \cdot \cos\alpha_i - d_{b_i}, \tag{18}$$

$$x_{u_{is}} = (d_{u_i} + d_{b_s}) \cdot \cos\alpha_{is} - d_{b_s} = D_{is} \cdot \cos\alpha_{is} - d_{b_s}. \tag{19}$$

From here, there results that:

$$L_{R_{b_s}} = R_{b_s} \cdot d_{b_s} + (D_s \cdot \cos\alpha_s - d_{b_s})t_{u_s} + (D_{is} \cdot \cos\alpha_{is} - d_{b_s})t_{u_{is}}, \tag{20}$$

$$L_{R_{b_i}} = R_{b_i} d_{b_i} + (D_i \cdot \cos\alpha_i - d_{b_i})t_{u_i}. \tag{21}$$

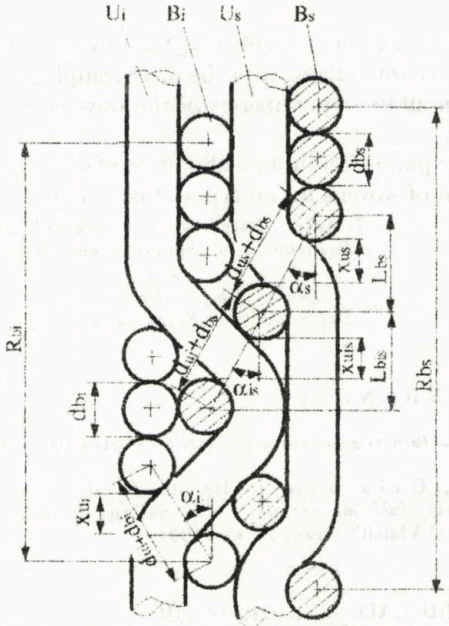


Fig. 4.– Double woven with ascending stitching.
Longitudinal section. Maximum technological thickness.

By replacing (20) and (21) consecutively in relation (2), the relations for the calculation of the weft system's compactness degree are obtained:

$$K_{b_s} = \frac{P_{b_s}[R_{b_s} d_{b_s} + (D_s \cos\alpha_s - d_{b_s})t_{u_s} + (D_{is} \cos\alpha_{is} - d_{b_s})t_{u_{is}}]}{R_{b_s}}, \tag{22}$$

$$K_{b_i} = \frac{P_{b_i}[R_{b_i} d_{b_i} + (D_i \cos \alpha_i - d_{b_i}) t_{u_i}]}{R_{b_i}}, \qquad (23)$$

where: tu_{is} is the number of passings of the inferior warp yarns through the yarns of the superior weft within a ratio; tu_s – number of passings of the superior and, respectively, inferior warp yarns through the yarns of the superior and, respectively, inferior weft yarns within a ratio; β_{is} - degree of curbing of the inferior warp, as a result of linking with the superior weft; α_{is} – degree of curbing of the superior weft, as a result of linking with the superior weft; xu_{is} – distance between two consecutive yarns of superior weft through which passes a yarn of inferior warp; α_i – degree of curbing of the inferior weft, as a result of linking, with the inferior weft; α_s – degree of curbing of the superior weft, as a result of linking, with the superior weft; xu_i, xu_s – distance between two consecutive yarns of superior and, respectively, inferior weft through which passes a yarn of superior and, respectively, inferior warp. Relations (13), (14) and (22), (23) are valid for all double wovens with ascending stitching, regardless of the alterance ratio between fibers or the similitude of the two parts.

5. Conclusion. The compactness degree is an index offering the woven's capacity of filling with yarns, at the same time characterizing it in the most complex way, as involving in to mathematical relation all basic parameters of the wovens, namely: linking, fineness and yarns' thickness.

The compactness degree is a basic parameter in the elaboration of some modern methods for computer-assisted design of wovens for all types of new materials.

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ALGORITM PENTRU CALCULUL GRADULUI DE COMPACTITATE A ŢESĂTURILOR DUBLE

I. Gradul de compactitate pentru ţesături duble cu însăilare ascendentă

(Rezumat)

Se prezintă un algoritm de calcul al gradului de compactitate pentru ţesături duble cu însăilare ascendentă, stabilindu-se expresia matematică a acestuia funcţie de parametrii de bază ai unei ţesături: densitatea de lungime şi desimea firelor, legătura şi materia primă.

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ALGORITHM FOR THE CALCULATION OF THE COMPACTNESS DEGREE FOR DOUBLE WOVENS

II. THE COMPACTNESS DEGREE FOR DOUBLE WOVENS WITH DESCENDING STITCHING

BY
GABRIEL CORNELIU CHINCIU, DANIEL CHINCIU and IRINA CRISTIAN

1. Introduction. The compactness degree for double wovens, to which stitching is performed either with the very yarns of layers or with special yarns of warp or weft, is calculated for each system of yarns belonging to the woven, with the folowing relations:

$$Ku_x = \frac{Pu_x L_{Ru_x}}{Ru_x}, \tag{1}$$

$$Kb_y = \frac{Pb_y L_{Rb_y}}{Rb_y}, \tag{2}$$

where x and y represent the system of warp yarns and, respectively, that of weft belonging to the double woven.

The compactness degree of the double woven is calculated by summing up of the compactness degree on systems of yarns, with relation:

$$Kt = \frac{\sum_{x=1}^{m} Ku_x + \sum_{y=1}^{n} Kb_y}{m+n} \tag{3}$$

where: m is the number of warp systems from the structure of the double woven, n – number of weft systems in the same woven.

2. Calculation of the compactness degree for double wovens with descending stitching, for an alternance ratio of 1: 1. The bloc diagram of the linking, the partial drawings as well as the assembly scheme of the linking are plotted in Figs. 1 and 2.

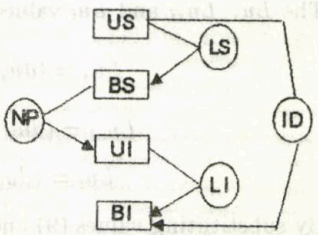

Fig. 1.– Bloc diagram of the double linking with descending stitching.

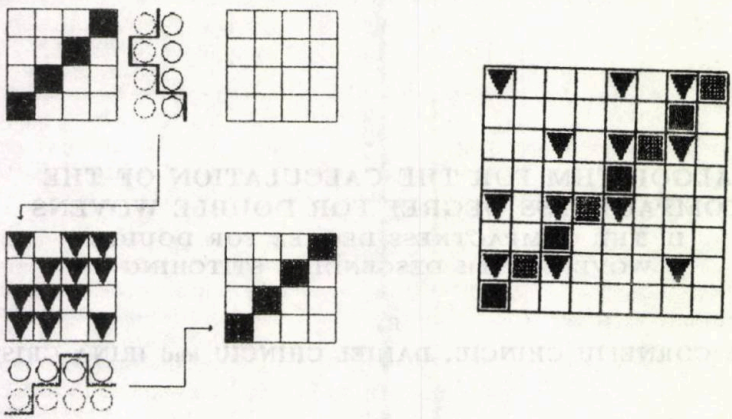

Fig. 2.– Double woven, descending stitching. Alternance ratio: 1Us:1Ui; 1Bs:1Bi.

3. Calculation of the compactness degree for the systems of warp. The compactness degree of the warp systems is calculated with relation (1), in which the length of the ratio in warp, L_R, for the two systems of warp yarns, at a maximum technological thickness, is calculated – as plotted in Fig. 3 – with the following relation:

$$L_{Ru_s} = Ru_s d_{u_s} + x_{b_s} t_{b_s} + x_{b_{si}} t_{b_{si}}, \tag{4}$$

$$L_{Ru_i} = Ru_i d_{u_i} + x_{b_i} t_{b_i}, \tag{5}$$

where:

$$x_{b_s} = L_{u_s} - d_{u_s} \tag{6}$$

$$x_{b_{si}} = L_{u_{si}} - d_{u_s} \tag{7}$$

$$x_{b_i} = L_{u_i} - d_{u_i} \tag{8}$$

The Lu_s, Lu_{si} and Lu_i values are calculate with relation:

$$Lu_s = (du_s + db_s)\cos\beta_s = D_s \cos\beta_s, \tag{9}$$

$$Lu_{si} = (du_s + db_i)\cos\beta_{si} = Dsi\cos\beta_{si}, \tag{10}$$

$$Lu_i = (du_i + db_i)\cos\beta_i = Di\cos\beta_i. \tag{11}$$

By substituting values (9) and (10) in relation (6) and (7) and then in (4) one may obtain the following relations:

$$L_{Ru_s} = Ru_s du_s + (Ds\cos\beta_s - du_s)tb_s + (Dsi\cos\beta_{si} - du_s)tb_{si}. \tag{12}$$

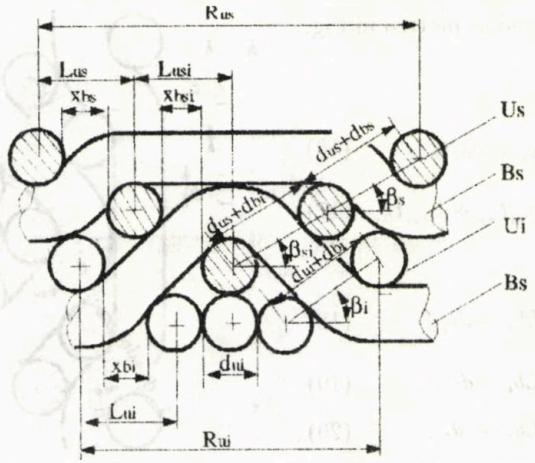

Fig. 3.– Double woven, descending stitching.
Cross section. Maximum technological thickness.

By substituting the value from (11) in (8) and then in (5), relation:

$$L_{Ru_i} = Ru_i du_i + (Di \cos \beta_i - du_i) tb_i \tag{13}$$

may be obtained.

The relations for the calculation of the compactness degree for the warp systems are obtained through the successive substitution of the values for LRu_s and LRu_i from relations (12) and, respectively (13) in (1), from which there result:

$$K_{u_s} = \frac{P_{u_s}[R_{u_s} d_{u_s} + (D_s \cos \beta_s - d_{u_s}) t_{b_s} + (D_{si} \cos \beta_{si} - d_{u_s}) t_{b_{si}}]}{R_{u_s}}, \tag{14}$$

$$K_{u_i} = \frac{P_{u_i}[R_{u_i} d_{u_i} + (D_i \cos \beta_i - d_{u_i}) t_{b_i}]}{R_{u_i}}, \tag{15}$$

where: D_{si} is the sum between the diameter of the yarns of superior warp, and diameter of the yarns of inferior weft; β_{si} – the degree of curling of the superior warp, as a result of the linking with inferior weft; tb_{si} – number of passings of the inferior weft yarns throught the yarns of the superior warp within a ratio.

4. Calculation of the compactness degree for the weft systems. For the weft systems, the compactness degree is calculated from relations (2), in which the length of the weft ratio for the two systems of yarns with maximum technological

thickness is calculated as plotted in Fig. 4, with relations:

$$L_{Rb_s} = Rb_s d_{b_s} + x_{u_s} t_{u_s}, \tag{16}$$

$$L_{Rb_i} = Rb_i d_{b_i} + x_{u_i} t_{u_i} + x_{u_{si}} t_{u_{si}}, \tag{17}$$

in which:

$$x_{u_s} = Lb_s - d_{b_s}, \tag{18}$$

$$x_{u_i} = Lb_i - d_{b_i}, \tag{19}$$

$$x_{u_{si}} = Lb_{si} - d_{b_i}. \tag{20}$$

The Lb_s, Lb_i and Lb_{si} values may be calculated with relations:

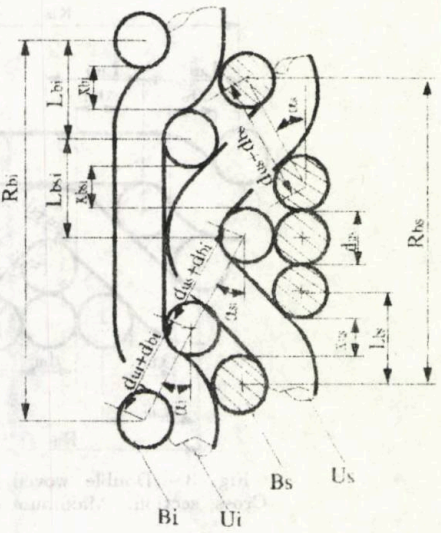

Fig. 4.– Double woven, descending stitching. Longitudinal section. Maximum technological thickness.

$$Lb_s = (d_{u_s} + d_{b_s}) \cos \alpha_s = D_s \cos \alpha_s, \tag{21}$$

$$Lb_i = (d_{u_i} + d_{b_i}) \cos \alpha_i = D_i \cos \alpha_i, \tag{22}$$

$$Lb_{si} = (du_s + db_i) \cos \alpha_{si} = D_{si} \cos \alpha_{si}. \tag{23}$$

Substituting values Lb_s from (21) into (18) and then in (16) the relation for calculating the length of the ratio in the weft for the superior linking may be obtained.

Substituting the values (22) and (23) into (19) and, respectively (20), and than in (2) may be obtained the relation for calculating the length of the weft ratio for the inferior linking:

$$L_{Rb_s} = Rb_s d_{b_s} + (D_s \cos \alpha_s - d_{b_s}) t_{u_s}, \tag{24}$$

$$L_{Rb_i} = Rb_i d_{b_i} + (D_i \cos \alpha_i - d_{b_i}) t_{u_i} + (D_{si} \cos \alpha_{si} - d_{b_i}) t_{u_{si}}. \tag{25}$$

The relations for the calculation of the compactness degree of the weft systems are obtained through the successive substitution of the values from (24) and (25) in relation (2), from which there results:

$$Kb_s = \frac{Pb_s \lfloor Rb_s d_{b_s} + (D_s \cos \alpha_s - d_{b_s}) \rfloor}{Rb_s}, \tag{26}$$

$$Kb_i = \frac{Pb_i \lfloor Rb_i d_{b_i} + (D_i \cos \alpha_i - d_{b_i}) t_{u_i} + (D_{si} \cos \alpha_{si} - d_{b_i}) t_{u_{si}} \rfloor}{Rb_i}, \tag{27}$$

in which: x_{s_1} is the degree of curling of the inferior weft as a result of linking with the superior warp; tu_{si} – number of passing of the superior warp yarns through the yarns of the inferior weft.

Relations (14) and (15) and also (26) and (27) are valid in all variants of the double wovens, with descending stitching regardless of the alternance ratio of the yarn systems and the parts similitude.

5. Conclusions. The calculation algorithm of the compactness degree disscused in the present study permits the establishment of the some metods for double wovens with descending stitching, as a function of the degree of compactness required, as a parameter defining a woven material in the most complete mode.

The value of the compactness degree depends both on the thickness and fineness (expressed through the diameter) of the yarn systems, as well as by the linking applied.

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ALGORITM PENTRU CALCULUL GRADULUI DE COMPACTITATE PENTRU ŢESĂTURI DUBLE
II. Gradul de compactitate pentru ţesături duble cu însăilare descendentă

(Rezumat)

Considerând gradul de compactitate un indice complex de caracterizare a ţesăturilor, se prezintă un algoritm de calcul al acestuia pentru ţesături duble cu însăilare descendentă, exprimându-se gradul de compactitate funcţie de parametrii de bază ai unei ţesături: densitatea de lungime şi desimea firelor, legătura şi materia primă.

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Secţia VIII
TEXTILE. PIELĂRIE

ALGORITHM FOR THE CALCULATION OF THE COMPACTNESS DEGREE FOR DOUBLE WOVENS

III. THE COMPACTNESS DEGREE FOR DOUBLE WOVENS WITH MIXED STITCHING

BY
IRINA CRISTIAN, DANIEL CHINCIU and GABRIEL CORNELIU CHINCIU

1. Introduction. The compactness degree for double wovens, to which stitching involves the layers' yarns or with special warp or weft fibers is calculated for each system of yarns entering the woven, with the following relations:

$$Ku_x = \frac{Pu_x L_{Ru_x}}{Ru_x}, \tag{1}$$

$$Kb_y = \frac{Pb_y L_{Rb_y}}{Rb_y}, \tag{2}$$

in which x and y represent the system of warp and, respectively, weft entering the double woven.

The compactness degree of the double woven is calculated by summing up the degrees of compactness on yarn systems, with relations:

$$Kt = \frac{\sum_{x=1}^{m} Ku_x + \sum_{y=1}^{n} Kb_y}{m+n} \tag{3}$$

in which: m is the number of warp systems in the structure of the double woven, n – number of weft systems in the same woven.

2. Calculation of the compactness degree for double wovens with mixed stitching, alternance ratio 1: 1, (LD–IMx). Figs. 1 and 2 plot graphically the linking's interlacing weave block diagram, as well as its partial and general scheme.

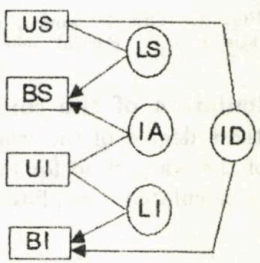

Fig. 1.– Block diagram of the double interlacing weave with mixed stitching.

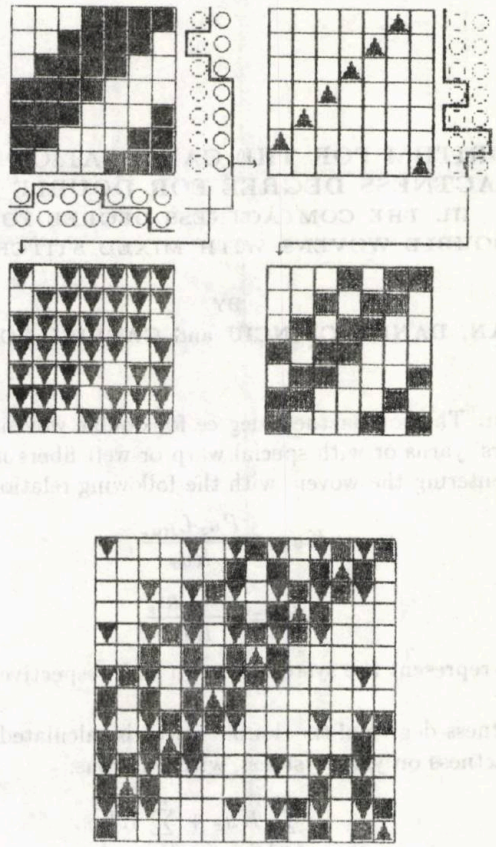

Fig. 2.– Double woven, mixed stitching. Alternance ratio: 1Bs : 1Bi; 1Us : 1Ui. Partial scheme. General scheme of the interlacing weave.

3. Calculation of the compactness degree for the warp system. The compactness degree of the warp system is calculated with relation (1) in which length of the warp ratio for the two warp systems for a maximum technological length, is calculated – as plotted in Fig. 3 – with the following relations:

$$L_{Ru_s} = Ru_s du_s + xb_s tb_s + xb_{si} tb_{si}, \tag{4}$$

$$L_{Ru_i} = Ru_i du_i + xb_i tb_i + xb_{is} tb_{is}, \tag{5}$$

in which:

$$xb_s = Lu_s - du_s, \tag{6}$$

$$xb_{si} = Lu_{si} - du_s, \tag{7}$$

$$xb_i = Lu_i - du_i, \tag{8}$$

$$xb_{is} = Lu_{is} - du_i. \tag{9}$$

The Lu_s, Lu_{si}, Lu_i and Lu_{is} values are calculated as follows:

$$Lu_s = (du_s + db_s)\cos\beta_s = D_s \cos\beta_s, \tag{10}$$

$$Lu_{si} = (du_s + db_i)\cos\beta_{si} = D_{si}\cos\beta_{si}, \tag{11}$$

$$Lu_i = (du_i + db_i)\cos\beta_i = D_i \cos\beta_i, \tag{12}$$

$$Lu_{is} = (du_i + db_s)\cos\beta_{is} = D_{is}\cos\beta_{is}. \tag{13}$$

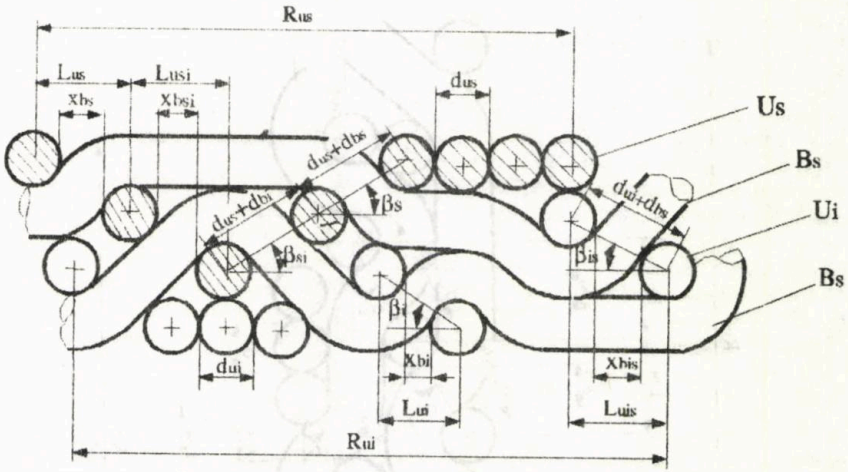

Fig. 3.– Double woven with mixed stitching. Cross section. Maximum technological length.

By substituting the values from (10) and, respectively, (11) in relation and (6) respectively (7) and then in (4) one gets the relation:

$$L_{Ru_s} = Ru_s du_s + (D_s \cos\beta_s - du_s)tb_s + (D_{si}\cos\beta_{si} - du_s)tb_{si}. \tag{14}$$

On substituting the values from (12) and, respectively, (13), in relation (8) and, respectively, (9), and then in (5) one gets the relation:

$$L_{Ru_i} = Ru_i du_i + (D_i \cos\alpha_i - du_i)tb_i + (D_{is}\cos\beta_{is} - du_i)tb_{is}. \tag{15}$$

On substituting the values from (14) and then from (15) in (1) the relations for the calculation of the compactness degree of the warp systems are obtain:

$$K_{u_s} = \frac{P_{u_s}[R_{u_s}d_{u_s} + (D_s \cos\beta_s - d_{u_s})t_{b_s} + (D_{si}\cos\beta_{si} - d_{u_s})T_{b_{si}}]}{R_{u_s}}, \qquad (16)$$

$$K_{u_i} = \frac{P_{u_i}[R_{u_i}d_{u_i} + (D_i \cos\beta_i - d_{u_i})t_{b_i} + (D_{is}\cos\beta_{is} - d_{u_i})t_{b_{is}}]}{R_{u_i}}, \qquad (17)$$

4. Calculation of the compactness degree for the weft systems. The compactness degree of the weft system is usually calculated with relation (2) in which the length of the weft ratio for the two systems of yarns with maximum technological length are calculated – as seen in Fig. 4 – with relations:

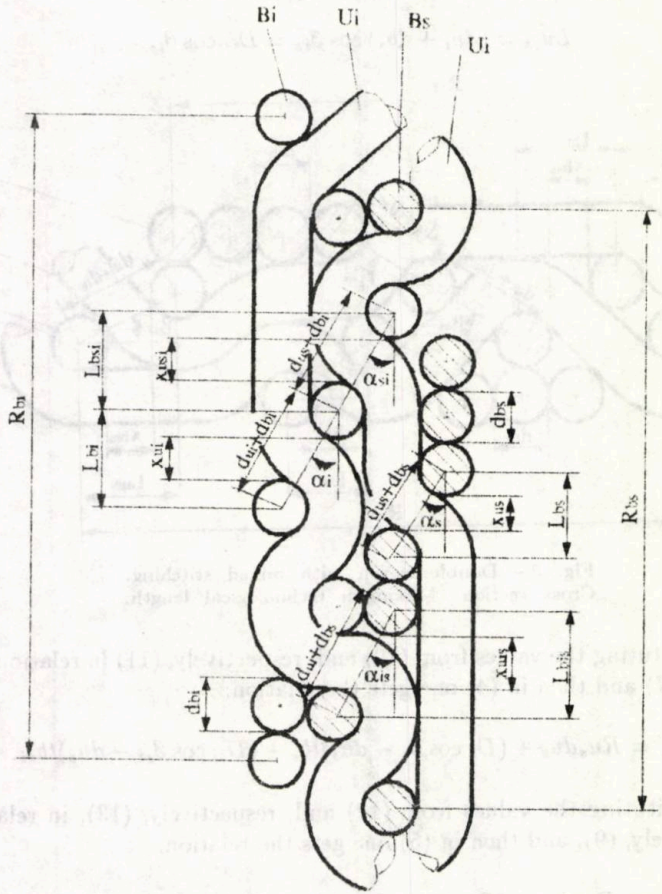

Fig. 4.– Double woven with mixed stitching.
Longitudinal section. Maximum technological thickness.

$$L_{Rb_s} = Rb_s d_{b_s} + x_{u_s} t_{u_s} + x_{u_{is}} t_{u_{is}}, \tag{18}$$

$$L_{Rb_i} = Rb_i d_{b_i} + x_{u_i} t_{u_i} + x_{u_{si}} t_{u_{si}}, \tag{19}$$

in which:

$$x_{u_s} = Lb_s - db_s, \tag{20}$$

$$x_{u_{is}} = Lb_{is} - db_s, \tag{21}$$

$$x_{u_i} = Lb_i - db_i, \tag{22}$$

$$x_{u_{si}} = Lb_{si} - db_i. \tag{23}$$

The Lb_s, Lb_{is}, Lb_i and Lb_{si} values are calculated with relations:

$$Lb_s = (du_s + db_s)\cos\alpha_s = D_s \cos\alpha_s, \tag{24}$$

$$Lb_{is} = (du_i + db_s)\cos\alpha_{is} = D_{is}\cos\alpha_{is}, \tag{25}$$

$$Lb_i = (du_i + db_i)\cos\alpha_i = D_i \cos\alpha_i, \tag{26}$$

$$Lb_{si} = (du_s + db_s)\cos\alpha_{si} = D_{si}\cos\alpha_{si}. \tag{27}$$

By substituting the values from (24) and, respectively (25) in relations (20) and respectively (21) and then in (18) one gets:

$$L_{Rb_s} = Rb_s d_{b_s} + (D_s \cos\alpha_s - d_{b_s})t_{u_s} + (D_{is}\cos\alpha_{is} - d_{b_s})t_{u_{is}}. \tag{28}$$

In a similar manner, on substituting the values from, (26) and, respectively (27) in relations (22) and, respectively (23) and then in (19) one gets:

$$L_{Rb_i} = Rb_i d_{b_i} + (D_i \cos\alpha_i - d_{b_i})t_{u_i} + (D_{si}\cos\alpha_{si} - d_{b_i})t_{u_{si}}. \tag{29}$$

On substituting the values from (28) and then from (29) in (2) the relations for the calculation of the warp systems' compactness degree may be calculated:

$$Kb_s = \frac{Pb_s[Rb_s d_{b_s} + (D_s \cos\alpha_s - d_{b_s})t_{u_s} + (D_{is}\cos\alpha_{is} - d_{b_s})t_{u_{is}}]}{Rb_s}, \tag{30}$$

$$Kb_i = \frac{Pb_i[Rb_i d_{b_i} + (D_i \cos\alpha_i - d_{b_i})t_{u_i} + (D_{si}\cos\alpha_{si} - d_{b_i})t_{u_{si}}]}{Rb_i}. \tag{31}$$

Relations (16) and (17) as well as (30) and (31), are valid in all variants of double wovens with mixed stitching.

5. Conclusion. The compactness degree expresses, as percent values, the occupation degree of the maximum capacity of compactness degree of a woven with yarns, considered as 100it is the index that characterizes a woven in the most complex way. Its mathematical relation includes all basic parameters of the woven, namely:

interlacing weave, fineness and the yarns' thickness, which explains the fact that the new methods for wovens' designing – considering the compactness degree – result in the obtainment of some highly rational wovens.

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ALGORITM PENTRU CALCULUL GRADULUI DE COMPACTITATE PENTRU ŢESĂTURI DUBLE
III. Gradul de compactitate pentru ţesături duble cu însăilare mixtă

(Rezumat)

Se stabileşte un algoritm de calcul al gradului de compactitate pentru ţesături duble cu însăilare mixtă funcţie de parametrii de bază ai unei ţesături: densitatea de lungime, desimea firelor, legătura şi materia primă, expresia matematică a gradului de compactitate constituind, în acelaşi timp, o bază de proiectare raţională a ţesăturilor.

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Secţia VIII
TEXTILE. PIELĂRIE

CONTRIBUTIONS TO THE STUDY OF THE STRIKING MECHANISMS OF THE RIGID JOINT ELEMENTS WHICH ENTER THE COMPONENCE OF SOME MACHINES USED IN FOOTWEAR MANUFACTURING

BY

DAN FLORIN CROITORU

1. Introduction. Joining machines with rigid elements (nails, tacks, rivets, etc.) used in footwear industry are provided with working elements and forced inserting mechanisms of the joint elements in the joint-to-be materials, respectively. The striking or the joining elements is usually done with the help or some dropping elements, their descend being done both under the action of their own weights and by means of the elastic force obtained by the expansion of an elastic element which has been compressed during the previous raising phase [1].

The raising and descending movements, respectively, of the striking element are obtained by means of some variable structure mechanisms which ensure the setting free of the striking element from the rest of the elements from the kinematic chain so that this should be able to descend independently [2]. If the raising movement can be studied by using the computation relations corresponding to the type of mechanism through which this movement is obtained, one cannot say the same thing about the descending movement at the end of which the intended technological effect is, in fact, accomplished. The specialized literature in which these mechanisms are presented do not offer the computation relations which could allow the exact determination of the kinematic and dynamic parameters, respectively, parameters which are important both for the proper designing of the mechanism and for the correct estimation of the technological effect.

This paper determines the movement law of the striking element during the descending phase; this law has been applied to the concrete case of the SVIT 02015/P5 tacks joining machine.

2. Establishing of the Movement Law of the Striking Element During the Descending Phase. One takes into account the striking element *1* (Fig.1) in a descending movement under the action of its own weight P and of the elastic force F exerted by the cylindric helical spring *2* which works at compression. If the friction

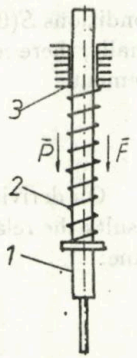

Fig. 1

force between the striking element *1* and the fixed guide *3* of the machine is neglected and if one notes the mass with M and the acceleration of the striking element with a, then on the basis of the fundamental equation of the translation movement dynamics of a solid body [3], one can write:

$$Ma = P + F \tag{1}$$

The weight P can be expressed function of the mass M and gravitational acceleration g; the elastic force F can be expressed function of the rigidity K of the helical spring and its compression f [4] so that the relation (1) becomes:

$$Ma = Mg + Kf \tag{2}$$

At the same time, if one takes into account the fact that the acceleration represents the second derivative of the space S traversed by the striking element in comparison with the descending time t and if one also considers the initial compression f_0 of the helical spring, then one obtains:

$$M\frac{\mathrm{d}^2S}{\mathrm{d}t^2} = Mg + K(f_0 - S) \tag{3}$$

This represents a quadratic differential equation of the following form:

$$M\frac{\mathrm{d}^2S}{\mathrm{d}t^2} + KS = Mg + Kf_0 \tag{4}$$

By solving this differential equation, the following function is obtained:

$$S = A\cos\left(\sqrt{\frac{K}{M}}t\right) + B\sin\left(\sqrt{\frac{K}{M}}t\right) + \frac{Mg + Kf_0}{K} \tag{5}$$

which contains the constants A and B which will be determined from the initial conditions $S(0) = 0$ and $v(0) = 0$, v being the speed of the striking element. Thus, finally, there results the time function that represents the motion law of the striking element:

$$S = \frac{Mg + Kf_0}{K}\left[1 - \cos\left(\sqrt{\frac{K}{M}}t\right)\right] \tag{6}$$

On deriving the displacement of the striking element as against the time, there results the relation which allows the computation of the speed function of the same time:

$$v = \frac{Mg + Kf_0}{K}\sqrt{\frac{K}{M}}\sin\left(\sqrt{\frac{K}{M}}t\right) \tag{7}$$

At the same time, on deriving the speed as against the time, the acceleration of the striking element is obtained:

$$a = \frac{Mg + Kf_0}{K} \cos\left(\sqrt{\frac{K}{M}}t\right) \tag{8}$$

3. The Kinematic Analysis of the Descending Phase of the Striking Element from the SVIT 020215/P5 Tacks Joining Machine. The cylindric helical spring from the SVIT 02015/P5 tacks joining machine has the following characteristics: number of coils $n = 10$; radius of the winding cylinder $r = 0.0015$ m; wire diameter $d = 0.004$ m; elasticity transverse modulus $G = 8.085 \cdot 10^{10}$ N/m^2. On the basis of these data, the determination of the rigidity K [4] of the helical spring can be:

$$K = \frac{G\mathrm{d}^4}{64r^3n} = 9580 \ \text{N/m} \tag{9}$$

On the basis of the relation (6) and on taking into account the maximum displacement of 0.032 m of the striking element, a descending time $t_c = 0.0128$ s is obtained. Thus, there results that the time t which represents the independent variable of the functions (6), (7) and (8) can obtain values ranging between zero and t_c; therefore, it is possible the determination of the kinematic parameters S, v and a which characterize the descending movement of the striking element. Thus in Table 1 there have been determined these parameters for three consecutive values of the time t in the mentioned range while on the basis of the obtained results the diagrams from Fig.2 have been plotted.

Table 1

t, [s]	0.0000	0.0032	0.0064	0.0096	0.0128
s, [m]	0.0000	0.0024	0.0092	0.0195	0.0320
v, [m/s]	0.0000	1.4703	2.7503	3.6067	4.1234
a, [m/s^2]	469.6400	439.2592	352.0475	233.2405	58.1576

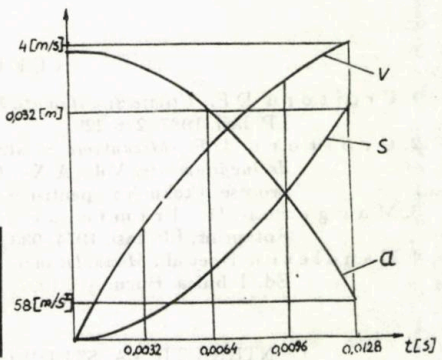

Fig. 2

A special importance from a technological view point has the knowledge of the speed of the striking element at the end of the movement, this being the moment when the impact with the joining element is produced. In the case when one can ascertain that the value of this parameter is not satisfying, one can proceed to an optimization computation of the mechanism running by varying the initial

compression f_0 of the helical spring. This thing can be accomplished, the machine being provided with a device allowing the carrying out of this adjustment.

On the assumption that the descend of the striking element would be performed up to the complete expansion of the helical spring (i.e., $S = f_0$), from the relation (6) one obtains $t = 0.01372$ s while from the relation (8) there results $a = 9.7$ m/s^2, a value aproximately equal to the gravitational acceleration g. This last result proves the validity of the relations determined in this paper because from this moment, the striking element would descend freely, only under the action of its own weight.

4. Conclusions. a) The main aim of this study is the determination of the law of motion of the striking element for the rigid joint elements, a law from which the relation allowing the computation of the speed and acceleration, respectively, during the descend phase result.

b) By appying the computation relations obtained in the concrete case of the striking element from the SVIT 02015/P5 machine, we could finally plot the diagrams which render evident the way the kinematic parameters of the striking element in this case vary.

c) By the contribution brought out in the accomplished study, one establishes the possibility of checking out by computation of the action exerted by the striking element on the joining elements, thus the estimation of the kinetic energy available in the moment of impact being possible.

d) The determined relations allow the deepening of the study on the striking mechanism by approaching some aspects aimed towards the optimization of the technological effect.

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CONTRIBUŢII LA STUDIUL MECANISMELOR DE BATERE A ELEMENTELOR DE ÎMBINARE RIGIDE CARE INTRĂ ÎN COMPONENŢA UNOR MAŞINI FOLOSITE LA FABRICAREA ÎNCĂLŢĂMINTEI

(Rezumat)

Prin studiul efectuat se determină legea de mişcare a organului de batere a elementelor de îmbinare rigide pe parcursul fazei de coborâre, fiind posibilă controlarea prin calcul a parametrilor cinematici sau, ulterior, a celor dinamici, în momentul impactului.

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Secţia VIII
TEXTILE. PIELĂRIE

ESTABLISHEMENT OF THE INFLUENCE OF SOME TECHNOLOGICAL FACTORS UPON THE RIGIDITY OF FOOTWEAR UPPER PART

BY

RODICA-SILVIA VOLOCARIU

1. General Remarks. In processes of footwear utilization, its upper part and coating are subjected to repeated bendings, which involves additional consumption of mechanical work for footwear's bending in the region of metatarsus – phalanx joints. On knowing that, generally, footwear's functions contribute to facilitating walking, its rigidity becomes of prime importance.

Rigidity is therefore defined as the solid bodies' property of not being deformed under the actions of the forces acting upon them [1].

The manner in which a certain material responds to stresses depends on its nature and specific properties, consequently its rigidity may be determined from the stresses recorded to bending, torsion, buckling.

The materials used for the fabrication of footwear upper part evidence an elastic-plastic behaviour to stresses. Also, the stresses to which they are subjected induce modification in the geometry of a material sample, reflecting, at a macroscopic level, the modifications occurring at the level of its intimate structure.

In conditions of experimental stresses applied over narrow domains, corresponding to the domains of the material's elastic behaviour, determination of rigidity may employ the classical relations for material's resistance [2].

Selecting stresses to bending as characteristic types among the other, the sample was tested versus a beam with rectangular section fixed at one end and driven – at the free end – by a bending force, rigidity was expressed with the following relation:

$$R = EI, \quad [\text{daNcm}^2], \tag{1}$$

where: R is rigidity of the material, [daNcm^2]; E – elasticity modulus of the material, [daN/cm^2]; I – inertion moment of the cross section, [cm^4],

$$I = \frac{bh^3}{12}, \quad [\text{cm}^4], \tag{2}$$

where: b is width of the sample; h – thickness of the sample.

The inertion moment of the rectangularty-shaped section, depending on the third power of the material's thickness, h, determines – theoretically – on doubling a material's thickness, its rigidity should increase 8 times.

Starting from this, formation of footwear assemblies of upper part and coating, through superposition and joining – in various ways – of 2 or more layers of material is expected to increase – to various extents – their rigidity.

Modification of rigidity, caused by modifications in the assemblies thickness and also in the methods of assembling applied, may be appreciated by means of a rigidity index – I_r – calculated as the ratio between the rigidity of the assembly obtained by simply doubling the sample or by doubling – assemblage, and the rigidity of the simple sample of material.

This index will be calculated in various ways, for putting into evidence either the simple or the cummulated effect of the factors influencing the value of the materials' rigidity.

Compared with the teoretical value, 8, the values obtained for the rigidity indices will reflect the rigidization tendency, thus permitting drawing of some final conclusions.

2. Experimental. For the experimental determination of the influence of certain technological factors (variation of thickness through superposition and the joining method employed for the assembly of footwear's upper part and covering) a leather substituent, of the SINAPA type, has been selected for upper part, together with a textile fabric for covering.

(30×100) mm rectangular samples have been cut, and then assembled, in the following conditions – superposition of 2 samples (doubling without assemblage), superposition and assembling either by sewing or by provisional fixing (gluing) of the covering, followed by sewing.

The simple samples and assemblies has been subjected to bending stress, under the previously mentioned conditions.

Rigidity has been determined on a device conceived and built by specialists of the Leather Department (described in [3]).

The device's clamp – permitting fixing of the sample or of the assembly, may be rotated with a crank, which modifies the initial (vertical) position of the embedding plane with various φ angles – as plotted graphically in Fig.1 (a and b).

The additional weight suspended at the free end of the sample (assembly) determines force $\overline{P}$, wich is decomposed into two compounds, $\overline{N}$ and $\overline{T}$, as seen from Fig.1 a and b, illustrating the following parameters:

$OA = l$ – initial length of the sample's (assembly's) free portion;

$OA' = l'$ – length of the sample's string, bended by the clamp's rotation at an angle of φ;

$AB = f$ – arrow measured at the sample's free end;

α – angle between the vertical line passing through the clamp's axis and direction of the OA string.

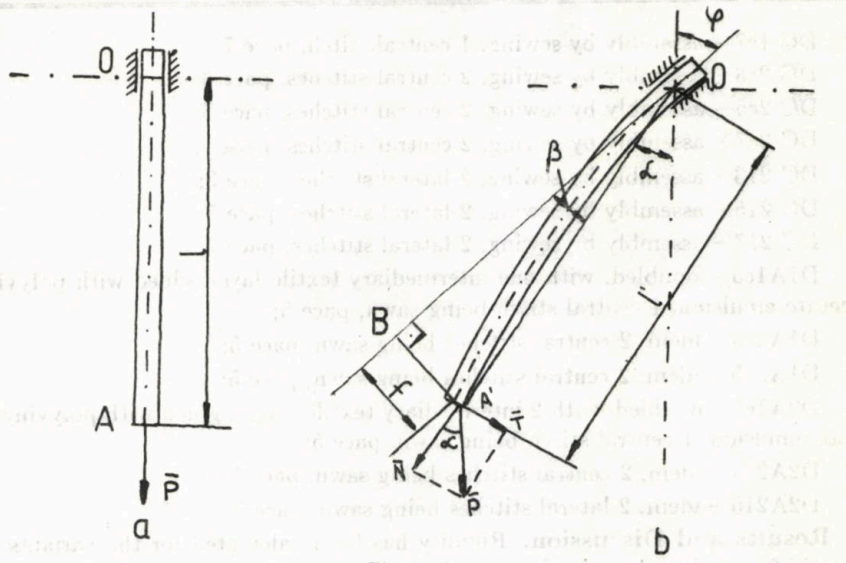

Fig. 1

Among these parameters, in the OAB rectangular triangle (reprezented in Fig.1 *b*) the following connecting relations are established:

$$T = P \sin \alpha, \tag{3}$$

$$f = OA \sin \beta = l' \sin \beta, \tag{4}$$

$$\beta = \varphi - \alpha, \tag{5}$$

$$R = \frac{Tl^3}{3f} = \frac{Pl^3 \sin \alpha}{3l' \sin \beta}. \tag{6}$$

As all determinations are performed in conditions in which the $Pl^3/3$ ratio represents a constant value, written as C, there results that:

$$R = C \frac{\sin \alpha}{l' \sin \beta}. \tag{7}$$

For getting rigidity values by applying relation (7), stresses to bending of 5 simple samples, both superposed (doubled and unassembled) and assembled, have been performed, which permitted putting into evidence the influence of the mentioned technological factors upon rigidity.

In view of their identification, these variants have been coded as follows:

S – simple sample;

D – superposed non-joined samples (doubled assembly);

DC 1c3 – assembly by sewing, 1 central stitch, pace 3;

DC 1c5 – assembly by sewing, 1 central stitch, pace 5;

DC 1c7 – assembly by sewing, 1 central stitch, pace 7;

DC 2c3 – assembly by sewing, 2 central stitches, pace 3;

DC 2c5 – assembly by sewing, 2 central stitches, pace 5;

DC 2c7 – assembly by sewing, 2 central stitches, pace 7;

DC 213 – assembly by sewing, 2 lateral stitches, pace 3;

DC 215 – assembly by sewing, 2 lateral stitches, pace 5;

DC 217 – assembly by sewing, 2 lateral stitches, pace 7;

D1A1c5 – doubled, with one intermediary textile layer, glued with polyvinylacetate emulsion, 1 central stitch being sawn, pace 5;

D1A2c5 – idem, 2 central stitches being sawn, pace 5;

D1A215 – idem, 2 central stitches being sawn, pace 5;

D2A1c5 – doubled, with 2 intermediary textile layers, glued with polyvinylacetate emulsion, 1 central stitch being sawn, pace 5;

D2A2c5 – idem, 2 central stitches being sawn, pace 5;

D2A215 – idem, 2 lateral stitches being sawn, pace 5.

3. Results and Discussion. Rigidity has been calculated for the variants obtained after application of stresses to bending and of measurements – for 3 values – of the clamp's rotation angle φ.

Table 1 centralizes the individual and average values of rigidity, calculated for $\varphi = 50°$, for all variants taken into study.

Table 1

Coded variant	Rigidity at $\varphi = 50°$ Ncm^2					Average rigidity Ncm^2
S	1.461	1.964	1.964	1.964	1.964	1.796
D	2.782	2.497	3.441	3.561	2.497	2.906
DC1c3	3.966	4.061	4.061	4.358	4.061	4.108
DC1c5	4.061	4.610	4.902	4.061	4.610	4.448
DC1c7	5.635	5.567	5.635	6.644	5.635	5.823
DC2c3	4.795	4.876	5.683	5.045	4.876	5.071
DC2c5	5.750	5.635	6.180	5.635	5.902	5.802
DC2c7	6.672	7.146	6.672	6.180	7.146	6.763
DC213	5.325	6.180	5.924	5.325	5.719	5.694
DC215	6.307	5.719	6.672	5.719	6.672	6.217
DC217	6.573	7.196	5.719	6.573	5.719	6.355
D1A1c5	6.086	6.046	5.857	6.086	5.816	5.973
D1A2c5	6.823	7.039	6.563	6.776	7.091	6.858
D1A215	7.093	6.579	7.039	6.521	6.821	6.803
D2A1c5	7.800	7.235	7.457	7.604	7.503	7.519
D2A2c5	10.218	11.108	10.570	10.902	10.807	10.721
D2A215	12.473	12.460	11.989	12.625	12.467	12.403

Tabelated average values of rigidity have been employed in the calculation of the rigidity indices I_{r1}, I_{r2}, I_{r3} and I_{r4}.

The calculation relations of the four rigidity indices, and the values obtained, are given in Table 2.

Table 2

Coded variant	Average rigidity Ncm²	$I_{r1} = \frac{R_D}{R_S}$	$I_{r2} = \frac{R_{DC}}{R_D}$	$I_{r3} = \frac{R_{DAc}}{R_{DC}}$	$I_{r4} = \frac{R_{DCs,i}}{R_{DC3}}$
S	1.796	–	–	–	–
D	2.906	1.618	–	–	–
DC1c3	4.108	2.204	1.413	–	–
DC1c5	4.448	2.476	1.532	–	1.082
DC1c7	5.823	3.242	2.003	–	1.417
DC2c3	5.071	2.818	1.738	–	–
DC2c5	5.820	3.240	2.002	–	1.147
DC2c7	6.763	3.765	2.327	–	1.334
DC213	5.694	3.170	1.959	–	–
DC215	6.217	3.461	2.139	–	1.092
DC217	6.355	3.538	2.186	–	1.116
D1A1c5	5.973	3.325	2.055	1.343	–
D1A2c5	6.858	3.814	2.359	1.174	–
D1A215	6.803	3.787	2.341	2.339	–
D2A1c5	7.519	4.186	2.587	1.094	–
D2A2c5	10.721	5.969	3.689	1.842	–
D2A215	12.403	6.905	4.268	1.995	–

Analysis of the average values of rigidity (Table 1) permits the following observations:

– increase in the rigidity of the assemblies joined by sewing, in parallels with increase of the sewing's thichness;

– varying rigidity values of the assemblies joined by sewing, as due to the stitches' position on the assembly's surface (either central – 1 or 2 – or lateral) explainable by the fact that, on stressing, joiging permits or not a slight sliding of the material's layers forming the assembly;

– increase of rigidity in assemblies formed by two joining methods (i.e., gluing and sewing), as a result of the cummulated effect of each method's influence.

The values of the last tabelated variants are over 8, which reflects the tendency towards rigidization.

The rigidity indices, calculated from the relations given in Table 2, take different values, the highest ones corresponding, again, to the assembly variants formed by the application of two joining methods.

The results obtained permit drawing of the following conclusions:

1. As the thickness of the joining sewing influences the assembly's rigidity, it should be maintained at an optimum value, so that it should not affect joining's resistance.

For the materials taken into study, the type of thread employed (SINTROM 65/3), as well as the needle's diameter (90), a thickness value 5 paces/cm is taken as optimum.

2. The arrangement and number of stitches within joinings also influence rigidity, a fact which should be considered in the concrete conditions of the assemblies forming and structuring; special attention should be therefore paid to their correlation with the samples form and direction of stress in the assemblies, so that the lowest influence should be exercised upon rigidity's increase.

3. On the manufacture of footwear's upper part and coverting, attention is to be paid to the cummulated influence of the nature, joining through sewing and adhesive type, together with application mode, so that the effect upon the assembly rigidity should be reduced.

4. A correct estimation of the influence exercised by the factors taken into study on the rigidity of joinings achieved through sewing or gluing permits a judicious utilization of each material in the process of production, for the obtainment of results corresponding to the domain of values required for this characteristic of footwear.

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STABILIREA INFLUENŢEI UNOR FACTORI TEHNOLOGICI ASUPRA RIGIDITĂŢII FEŢELOR ÎNCĂLŢĂMINTEI

(Rezumat)

Rigiditatea încălţămintei este o caracteristică importantă a acesteia, contribuind la uşurarea mersului.

În cadrul lucrării se urmăreşte punerea în evidenţă, pe cale experimentală, a acţiunii simple sau cumulate a unor factori tehnologici variabili asupra rigidităţii ansamblului feţe–căptuşeli de încălţăminte într-un caz particular.

Rezultatele obţinute stau la baza formulării unor concluzii cu utilitate practică.

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Secţia VIII
TEXTILE. PIELĂRIE

L'INFLUENCE DU RÉGIME DE THERMOFIXATION SUR LES PROPRIÉTÉS PHYSICO-MÉCANIQUES DU CUIR SYNTHÉTIQUE EN VUE DE L'ASSURANCE DE LA FIABILITÉ DES FORMES SPATIALES

PAR

FLORENTINA HARNAGEA et CORNELIA IONESCU

1. Des considérations théoriques. À la fabrication des produits de chaussure, pour l'ensemble supérieur, on emploie souvent des matériaux synthétiques dont les propriétés sont impliquées dans la qualité du produit fini [1], [2].

Les propriétés physico-mécaniques, conditionnées par les particularités structurales des matériaux, à côté des particularités higiéniques et thermiques, assurent le comportement dans le processus de fabrication et le confort dans l'emploi du produit [4].

Dans le processus de fabrication, les dessus de la chaussus sont tensionnées d'une telle manière qu'elles prennent la forme spatiale complexe de l'embauchoir et qu'elle soit assurée la fiabilité de la forme après l'extraction de l'embauchoir du produit fini et surtout pendant son exploitation [1], [3].

La formation spatiale sous l'action de la sollicitation de traction se réalise dans la plus grande mesure par la création des déformations rémanentes dans la structure de la matière [1]. Pour que la forme spatiale conférée au semifabriqué dans le processus de formation, soit plus stable dans le comportement, il est nécessaire qu'une partie plus grande de la déformation totale se transforme en déformation plastique [1], [2], étant connu le fait que la déformation totale se compose de la déformation élastique et la déformation plastique.

Dans les conditions du maintien dans l'état tensionné à la déformation constante, a lieu un relâchement des tensions dans la matière, comme la suite du réaranjement des éléments structuraux et en même temps l'augmentation de la déformation rémanente à la suite de l'établissement de la structure en état déformé [1], [3].

En vue de l'assurance de la fiabilité des formes spatiales sur les propriétés physico-mécaniques des matériaux, influencent une série de paramètres technologiques à savoir: le degré de déformation du matériel, la durée du maintien en état tensionné, la température et le temps de thermofixation, etc. [3], [4].

Par rapport à ceux mentionnés en haut, dans ce travail on présente les résultats de la recherche concernant l'influence significative du temps et de la température de thermofixation sur la grandeur de la déformation rémanente, dans le processus

de formation spatiale du cuir synthétique sur le support textile immersé.

2. La partie expérimentale. En vue de la réalisation des expérimentations on a employé le cuir synthétique à support textile immersé en solution de polyuréthanique, à pellicule de polyuréthanique – SINAPA – avec les caractéristiques suivantes: la grosseur δ=1,1 mm, allongement au déchirement ε_r=14-18% et effort unitaire au déchirement σ_r=4-8 N/mm^2.

La fait que les dessus de chuassure constituent un ensemble de 2-3 matériaux qui doivent être formés ensemble dans le processus de tirage sur l'embauchoir, on a réalisé des expérimentations sur des éprouvettes simples que sur des és que sur des éprouvettes en système c'est-à-dire doublées à méchine et à toile employée couramment au placage des dessus de chaussure. Les éprouvettes employées pour des déterminaisons (20×120 mm) ont été prélevées à la longueur parallèle à la direction de la chaîne du support textile, à la longueur du matériel et ensuite soumises à la sollicitation de traction jusqu'à l'obtention de la déformation totale imposée, à differents regimes de thermofixation.

L'allongement des éprouvettes sous l'effet de la force d'étendue a été de 10%, respectif de 15% étant considérée suffisante pour la moulage sur forme des dessus de chaussures en cuir synthétique.

Les éprouvettes, tensionnées à des régimes différents de thermofixation (par la variation du temps et de la température de thermofixation) ont été maintenues en état tensionné à la déformation constante imposée dans l'atmosphère libre, pendant 180 minutes.

La déformation rémanente a été mesurée à de differents temps de l'extraction à l'état tensionné à savoir, à trente minutes, vingt-quatre, quarante-huit heures et soixante-douze heures.

En vue de la comparaison des résultats, on a réalisé des expérimentations avec des éprouvettes tensionnées dans des conditions normales.

3. Résultats et discussions. La variation de la déformation rémanente en fonction du régime de thermofixation auquel ont été soumises les éprouvettes en état tensionné qui a été mesuré aux temps différents de l'extraction de l'état tensionné dans le Tableau 1.

Considérant l'établissement de la forme spatiale après soixante-douze heures de l'extraction de l'état tensionné dans la Fig.1, on représente la variation de la déformation rémanente en fonction du temps de thermofixation, correspondante à une déformation totale imposée et à la température dont on a réalisé la thermofixation.

Analysant les valeurs obtenues de la déformation rémanente au cuir synthétique du type „Sinapa", aussi comme la représentation graphique de la Fig.1, on constate les faits suivants:

– la déformation rémanente (plastique) grandit avec l'accroissement du temps de thermofixation, de la température de thermofixation et du degré de déformation du matériel pour les éprouvettes simples et pour les éprouvettes en système;

– les éprouvettes soumises aux traitements de thermofixation présentent des valeurs supérieures de la déformation rémanente envers les éprouvettes tensionnées

Tableau 1

La nature des éprouvettes	ε_t [%]	T [°C]	t [min]	ε_r, [%] 1/2 h	24 h	48 h	72 h
des éprouvettes simples (Sinapa)	10	–	–	0,7	0,4	0,2	0,1
		100	1	5,83	5,16	4,93	4,55
			7	6,73	6,26	5,86	5,46
			14	7,02	6,91	6,42	5,79
		140	1	6,23	5,37	4,96	4,78
			7	7,03	6,86	5,87	5,56
			14	7,35	7,17	6,43	6,12
	15	–	–	1,5	0,9	0,5	0,4
		100	1	7,63	6,93	6,42	6,20
			7	8,43	7,36	7,03	6,86
			14	8,98	8,33	7,62	7,16
		140	1	8,31	7,82	7,33	6,50
			7	8,73	8,21	7,71	7,15
			14	9,28	8,57	7,93	7,56
des éprouvettes en système (Sinapa+méchine+toile)	10	–	–	0,5	0,3	0,2	0,1
		100	1	7,94	7,43	7,15	6,60
			7	8,51	7,80	7,53	7,30
			14	8,83	8,40	8,14	7,67
		140	1	8,49	8,03	7,47	7,23
			7	8,67	8,27	7,96	7,76
			14	9,01	8,85	8,43	8,16
	15	–	–	2,3	1,8	1,1	0,7
		100	1	9,76	9,26	8,86	8,73
			7	9,96	9,66	9,54	9,41
			14	10,46	9,95	9,64	9,53
		140	1	9,86	9,56	9,28	9,03
			7	10,13	9,95	9,73	9,53
			14	10,76	10,85	10,10	9,77

Notation: ε_t – la déformation total, T – la température de thermofixation, t – le temps de thermofixation, ε_r – la déformation rémanente mesurée d'après des temps différents de l'extraction de l'état tensionné (d'après 1/2 h; 24 h; 48 h; 72 heures).

dans des conditions normales. On met en évidence, une accroissement de la déformation rémanente, à 6,02% dans le cas des éprouvettes simples et à 8,06 dans le cas des éprouvettes en système à ε_t=10%, t=14 minutes et T=140°C;

– la valeur maximale de la déformation rémanente à la même valeur de la déformation totale imposée est obtenue pour les éprouvettes en système à des valeurs supérieures du temps et de la température de thermofixation.

4. Conclusions. 1. Pour le cuir synthétique du tipe „Sinapa", les traitements de thermofixation sont absolument nécessaires en vue de l'accroissement de la déformation rémanente, respectif de la capacité de se maintenir la forme après l'éloignement du poids qui a produit la déformation.

2. Les valeurs concrètes attribuées pour la température de thermofixation ont eu comme but principal l'accroissement de la déformation plastique qui est décissive dans le maintien de la forme de chaussure et de son aspect commercial.

3. À la base des résultats obtenus, dans des conditions industrielles, on adoptera ce régime-là de thermofixation qui n'influence négativement la productivité du

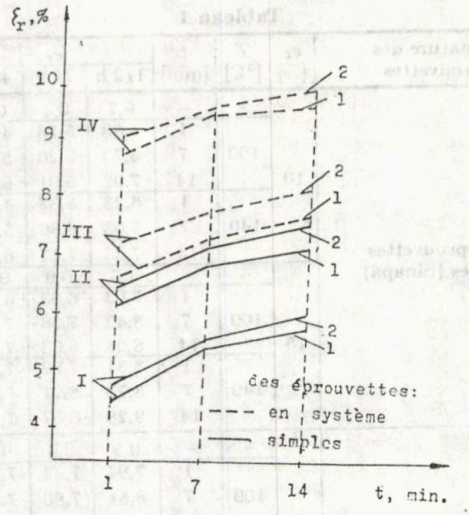

Fig. 1.– La variation de la déformation rémanente en fonction du temps de thermofixation. I, III – ε_t=10%; II, IV – ε_t=15%; 1 – T=100°C; 2 – T=140°C.

travail et qui permette un bon établissement dimensionnel par la réduction de la déformation élastique du matériel en faveur de la déformation rémanente.

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INFLUENŢA REGIMULUI DE TERMOFIXARE ASUPRA PROPRIETĂŢII FIZICO-MECANICE ALE PIELII SINTETICE ÎN VEDEREA ASIGURĂRII FIABILITĂŢII FORMELOR SPAŢIALE

(Rezumat)

Sunt prezentate rezultatele cercetării privind influenţa semnificativă a timpului şi temperaturii de termofixare asupra mărimii deformaţiei remanente în vederea asigurării fiabilităţii formelor spaţiale, la pielea sintetică pe suport textil imersat – tip Sinapa – utilizată frecvent la confecţionarea produselor de încălţăminte.

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Secţia VIII
TEXTILE. PIELĂRIE

NEW POSSIBILITIES FOR IMPROVING THE DYEING FASTNESS ON CELLULOSE FIBRES BY MEANS OF POLYFUNCTIONAL REACTANTS

BY

AUGUSTIN MUREŞAN, M. VAŢĂ, LUCIA TĂTARU, RODICA MUREŞAN and CRISTOFOR I. SIMIONESCU

1. Introduction. As early as the introduction of reactive dyes in technical applications, intense researches have been devoted to the discovery of some new types of covalent bonds between dye and fibre. The covalent bonds formed between the carbon atoms of the reactive nucleus from the dye and the oxygen atom's in cellulose may be achieved through either substitution or nucleophilic addition. Both substitution and nucleophilic addition have a common origin-namely, formation, within the reactant (reactive dye) of a positively-charged carbon, reacting with cellulose's anion [1].

The investigations on the nature of the reticulation-dye or reticulation-cellulose agent bond led to the conclusion that it is a covalent one. Therefore, a material dyed according to this procedure will not be dissolved in copper-ammoniacal solution, while the extraction of the dye – fixed by means of the reactant – is not possible through boiling with an aqueous solution of DMF [2].

Several agents of cellulose reticulation confer improved fastness to dyeing, in treatments in which, nevertheless, fastness to light in considerably influenced by the reticulation agent's nature [3].

2. Experimental. The present paper discusses new possible ways for improving the fastness of dyeings on cellulose fibres, with Polyfunctional reactants [4]. A bleached 100% cotton fabrics has been employed in experiments, in dyeings with three direct dyes, as follows: Direct red 2 (C.I. 25500), Direct blue 6 (C.I. 22610) and Direct green 6 (C.I. 63029), in the following experimental conditions: 3% direct dye, 10% NaCl, hydromodule 1:50, temperature 98°C, duration 30 minutes.

After washing the samples with both warm and cold water, and drying at room temperature, one of them has been kept as reference (untreated), the other ones being subjected to treatments with a series of Polyfunctional reactants [5]. Other two sets of dyed samples have been treated with a synthesised bireactive bicationic product [6], as follows: x% bicationic bireactive product (x=1; 3), 10 g/l Na_2CO_3, hydromodule 1:30, temperature 70°C, duration 40 minutes, then the samples have

been washed with cold water and dried at room temperature. Further on, a series of tests has been initiated on both treated and untreated samples, the amount of dye fixed through the reactant – as expressed by the fixation yield and dyeings fastness – being determined.

2.1. dye Fixed Through the Reactant. The dye fixed covalently on the fibre, through the reactant – was determined as the difference between the total amount of dye in the fibre and the non-fixed one. The amounts have been determined by extraction of dyes from the dyed – both treated and untreated – samples, in a DMF/water solution (volumetric ratio: 1:1), on boiling for 4 hours. Concentrations of dyes in the solutions employed were determined photocolorimetrically, after plotting of the reference curves. The results obtained for dyeings with the three dyes are presented in Table 1.

A first conclusion that may be drawn in that the fixation yield differs from one dye to another while, for the same dye, it depends on the reactant employed.

Table 1

Influence of the Reticulation Agent up on the dye's Fixation Yield

Sample	Products	Direct Red 2	Direct Blue 6	Direct Green 6
1	Viopret TR	80	51	48
2	Depremol G	84	80	82
3	Indosol CR	64.5	98	59
4	Reactant G_1	64.5	89.3	70.7
5	bireactive bicationic product 1%	16.2	32.5	26.3
6	bireactive bicationic product 5%	48.6	87.4	65.7

The influence of the dye's structure on the fixation yield can be only discussed as correlated with the structure of the reactants employed:

– the Viopret agent, with two functional groups of the OH-type and shoring mainly a self-reticulation action;

– Depremol G, with 4 functional groups of the OH-type, acting both as reticulation and self-reticulation agent, manifests much more uniform fixation of dyes;

– for the Reactant G_1, acting exclusively as reticulation agent, the fixation yield depends considerably on the structure of the dyes employed for dyeing;

– Indosol CR, with 4 functional groups – three of which for reticulations – while the fourth, a cationic one, evidences different fixation yield, as depending on the dye's structure.

In the case of Direct Red 2 and Direct Green 6 with 2 nucleophilic and 2 anionic groups, the fixation yield is of 50-60% while, for the Direct blue 6, with four nucleophilic and four sulfonic groups, the yield exceeds 90%.

– finally, by the utilisation's of the bireactive bicationic product – a tetrafunctional product – the fixation depends both on the dye's structure and on the amount of product employed in the after treatments bath. Consequently, with increasing the product's concentration, the fixed amount of dye increases for all dyes utilised. The highest yield is attained for direct blue, followed by direct green and direct red.

In a similar manner to the Indosol Cr product, besides fixing the dye through covalent bonds, the bicationic bireactive product, forms also electrochains with the anionic group in the dye's structure, which is reflected in improved fastness of dyeings during wet treatments. Nevertheless, the amount of bicationic bireactive product is much more reduced that involved in products with crease-resist effect, too.

2.2. Dyeing Fastness. In treatments aimed at improving the fastness of dyeings with direct dyes, selection of the products should have in view, too, the modification that may appear – in the dyed samples – as a result of the reticulation agent – dye interaction. Thus, it might be possible that a certain product should induce improvement in fastness along with essential modifications in colour – obviously, such products are not recommended. That is why, application of such treatments should consider first the modifications that might affect colour.

2.2.1. Colour modifications, resulted from treatments with polyfunctional reactants are presented – as colour differences – in Table 2.

Table 2

Colour Differences (ΔE) in Treatments with Polyfunctional Reactants

Sample	Products	Direct Red 2	Direct Blue 6	Direct Green 6
1	Untreated	0	0	0
2	Indosol CR	32.25	7.11	27.11
3	Reactant G_1	19.81	13.80	8.58
4	Depremol G	28.53	4.75	24.66
5	Viopret TR	99.62	10.97	13.76
6	bireactive bicationic product 1%	2.90	5.87	13.27
	bireactive bicationic product 1%	4.74	15.77	20.15

The difference in colour (ΔE) has been determined, comparatively with the untreated (reference) sample, by the CIELAB [7],...,[9], method adopted in Romania, as well. The above data permit the following conclusions:

– treatments with polyfunctional reactants modify the colour of the dyed samples;

– the observed colour differences depend both on the nature of the reactant employed and on the dye's structure;

– out of the products employed for dye's fixation by means of reactants, Viopret TR is not recommended in dyeings with direct red, as modifying considerably the colour, which practically becomes another.

Fastness properties values to various stresses are listed in Tables 3 to 6.

2.2.2. Wash Fastness. The values are presented in Table 3.

Utilisation of reactants improves wash fastness values, best results being obtained in treatments with bicationic bireactive products, a case in which maximum are obtained at concentrations of 3%.

2.2.3. The Perspiration Fastness. Determinations have made for both alkaline and acid perspiration, the results being given in Table 4.

Table 3
Wash Fastness at 40° C

Sample	Products	Direct Red 2			Direct Blue 6			Direct Green 6		
1	Untreated	4	2–3	4	4	4–5	2–3	4	3	4
2	Reactant G_1	4–5	3	3–4	4–5	5	4	4–5	4	4–5
3	Viopret TR	4–5	4	3–4	4–5	4	5	5	3–4	4–5
4	Indosol CR	4–5	3–4	4	4–5	4–5	5	4–5	3–4	4–5
5	Depremol G	4–5	3–4	3–4	4–5	5	4	4–5	4	4–5
6	bireactive bicationic prod. 1%	4	3	4	5	5	5	5	5	5
	bireactive bicationic prod. 5%	5	5	5	5	5	5	5	5	5

Table 4
The Perspiration Fastness

Alkaline perspiration

Sample	Products	Direct Red 2			Direct Blue 6			Direct Green 6		
1	Untreated	4–5	2–3	2	5	4–5	2–3	4	4	3
2	Reactant G_1	3–4	4–5	4	4–5	5	4	5	5	4–5
3	Viopret TR	2	4	3–4	4	5	4–5	5	5	5
4	Indosol CR	4	5	4	5	5	5	5	5	5
5	Depremol G	4	3–4	3	5	5	4	5	5	4–5
6	bireactive bicationic prod. 1%	4	3	4	5	5	5	5	5	5
	bireactive bicationic prod. 5%	5	5	5	5	5	5	5	5	5

Acid perspiration

Sample	Products	Direct Red 2			Direct Blue 6			Direct Green 6		
1	Untreated	4–5	2–3	2	4–5	5	2–3	4–5	4–5	3–4
2	Reactant G_1	4	4–5	4–5	4–5	5	4	5	5	5
3	Viopret TR	2	4–5	4	4	5	4–5	4–5	5	5
4	Indosol CR	4	5	5	5	5	5	5	5	5
5	Depremol G	4	3–4	3–4	5	5	4	5	5	5
6	bireactive bicationic prod. 1%	4–5	5	5	5	5	4–5	5	5	5
	bireactive bicationic prod. 5%	4–5	5	5	5	5	5	5	5	5

2.2.4. The Light Fastness. Light fastness value have been determined at artificial light, the samples being exposed for 10 hours at Xenotest. The results obtained are given in Table 5.

The above data evidence the following:

– the fastness to light is modified in treatments with polyfunctional reactants;

– the best fastness to light value are obtained with Indosol CR and Reactant G_1, while the lowest ones with Viopret TR;

– aftertreatments with bicationic bireactive product does not improve fastness light of the dyes employed.

Table 5
The Light Fastness

Sample	Products	Direct Red 2	Direct Blue 6	Direct Green 6
1	Untreated	2	3	3
2	Reactant G_1	2	3–4	3–4
3	Viopret TR	1–2	2–3	2–3
4	Indosol CR	2–3	3–4	4
5	Depremol G	2–3	3–4	3
6	bireactive bicationic product 1%	2	2–3	3–4
	bireactive bicationic product 1%	2	2	3

2.2.5. The Fastness to Rubbing. The data in Table 6 show that:
- the fastness value to dry rub are not modified;
- the fastness value to wet rub are improved.

Table 6
Fastness to Rubbing

Fastness to dry rubbing

Sample	Products	Direct Red 2	Direct Blue 6	Direct Green 6
1	Untreated	4 – 5	5	5
2	Reactant G_1	4 – 5	5	5
3	Viopret TR	4 – 5	5	5
4	Indosol CR	4 – 5	5	5
5	Depremol G	4 – 5	5	5
6	bireactive bicationic product 1%	4 – 5	5	5
	bireactive bicationic product 1%	4 – 5	5	5

Fastness to wet rubbing

Sample	Products	Direct Red 2	Direct Blue 6	Direct Green 6
1	Untreated	3 – 4	5	4 – 5
2	Reactant G_1	4	5	5
3	Viopret TR	4	5	5
4	Indosol CR	4	5	5
5	Depremol G	3 – 4	5	5
6	bireactive bicationic product 1%	4	5	4 – 5
	bireactive bicationic product 1%	4	5	4 – 5

3. Conclusion. The above described investigations were aimed at improving the fastness properties of cellulose fibers to dyeings with direct dyes.

i. The amount of dyes, fixed through covalent bonds, by means of polyfunctional reactants, depends bothe one the reticulation agent's nature and the dye's nature and the dye's chemical structure;

ii. The bireactive bicationic product may be employed as well, in the aftertreatments of dyeing, when it acts as a polyfunctional reactant;
iii. Consequently, dyeing aftertreatments which a bireactive bicationic product show improved fastness value – comparatively with the non treated ones – on washing, rubbing and perspiration, while to light is slightly diminished or unchanged;
iv. The fastness values of aftertreatments dyeing are generally higher or equal to those obtained with Indosol CR and Reactant G_1;
v. Selection of reactants should consider the colour modifications induced by the reticulation agent-dye reaction.

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NOI POSIBILITĂŢI DE ÎMBUNĂTĂŢIRE A REZISTENŢELOR VOPSIRILOR PRIN INTERMEDIUL REACTANŢILOR POLIFUNCŢIONALI

(Rezumat)

Se prezintă rezultatele obţinute în urma unor tratamente cu reticulanţi polifuncţionali asupra unor materiale vopsite cu trei coloranţi direcţi. În paralel se utilizează şi un produs cationic bireactiv. Se determină cantitatea de colorant legat covalent prin intermediul reactanţilor, diferenţa de culoare şi rezistenţele vopsirilor.

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Secţia VIII
TEXTILE. PIELĂRIE

CONTRIBUTION À LA CONNAISSANCE DES MODIFICATIONS DIMENSIONNELLES DES TISSUS SOUMIS À LA CONTRACTION PENDANT LES PROCESSUS D'ENNOBLISSEMENT TEXTILE

PAR

MARIN DINU et VALERIA NISTOR

1. Introduction. Les facteurs qui modifient les dimensions des textiles sont étroitement liés entre eux. Ils apparaissent à la matière première qui s'usine pendant le processus d'ennoblissement et à l'utilisation pratique de ces produits. Les outilages employés dans le production, spécialement ceux du processus d'ennoblissement, produisent à peu près sans exception des tensions qui apparaissent, d'habitude comme résistance à la traction du tissu. Malgré les efforts pour réduire ces tensions, seulement un nombre très réduit de mesures ont pu être réalisées avec succès, [1].

L'efficacité de quelques mécanismes comme celui d'avance de quelques machines textiles, dépend de la capacité caractéristique du tissu de revenir à l'état initial quand la tension est éliminée. Pourtant, normalement, l'état initial du tissu n'est pas atteint. Cet effet peut être obtenu seulement dans des conditions particulières et exclusivement à l'aide de machines spéciales à contracter avec lesquelles le problème de la contraction peut être abordée d'une manière tout à fait nouvelle.

2. Considerations théoriques. Comme on le sait déjà, suite à des traitements thermiques [2] le gonflement des fibres détermine une modification de la tension dans le tissu. Quand on humidifie, un gonflement des fibres se produit dans la direction axiale, comme gonflement longitudinal, ce qui a pour conséquence un allongement du fil et un gonflement des fibres dans la direction transversale (gonflement transversal), qui se manifeste comme un rétrécissement du fil. Le gonflement transversal étant un multiple du gonflement longitudinal, celui-ci peut pratiquement être ignoré comme grandeur.

Le gonflement transversal ne produit pas toujours une modification de la longueur du fil. Cette modification de la longueur du fil dépend de la structure du tissu, quand dans le tissu il y a assez d'espace libre pour le gonflement des fibres.

Par conséquent, pour les tissus avec des fils à faible torsion et à petite épaisseur, d'habitude, il n'existe pas de modifications dimensionnelles.

En revanche, pour une structure du tissu avec des fils plus torsionnés et avec une plus grande épaisseur, le gonflement transversal détermine une modification dimensionnelle. L'augmentation de la tension ou l'apparition d'un état d'équilibre dépend de la géométrie et de la structure du tissu.

Si la distance entre les fils d'un système d'armure se réduit, il suit une compression de l'autre système de fils. Cette force doit vaincre une plus grande résistance, dont la grandeur correspond à la valeur avec laquelle le tissu est plus épais dans l'autre système d'armure. La sphère de la contraction due au gonflement des fibres

sera déterminée à la fin par le direction où s'installe l'équilibre des forces. On peut supposer que dans les tissus plus rares les forces de tension résultées par le gonflement des fibres sont plus grandes que les forces de contraction.

Les tissus avec un certain toucher plein réduisent petit à petit la différence des forces qui agissent dans de différentes directions à la suite dú gonflement des fibres. On peut constater qu'à partir d'un certain toucher plein du tissu il n'apparait plus de contraction provenant du gonflement des fibres. L'équilibre des forces agissant dans de différentes directions conduit aussi à l'augmentation du toucher plein du tissu. Par là, la résistance qui comprime les systèmes d'armure n'augmente pas.

Il est nécessaire que les fils s'allongent aux points de croisement entre les fils de trame et les fils de chaine; toutefois, étant donné que les forces nécessaires à la réalisation d'une tension manquent, les fils seront déplacés dans la direction de la plus faible résistance. Cette possibilité existe par le rapprochement réciproque des fils dans le tissu, ce qui se manifeste comme contraction du tissu dans les deux directions.

La plupart des tissus modifient leurs dimensions dans l'eau ou dans des solutions aqueuses à cause de l'humidité. Quoique la contraction des tissus soit un processus assez compliqué, une examination attentive peut déterminer les principaux facteurs qui en sont responsables:

- les caractéristiques physico-chimiques des fibres du tissu;
- la structure et l'organisation géométrique des fibres dans le fil;
- la structure et le groupement géométrique des fils dans le tissu;
- le processus technologique d'obtention du tissu à parter de la filature jusqu'à l'ennoblissement.

Une importance particulière est detenue par les forces et tensions qui influencent le tissu ou le fil surtout pendant les opérations technoligiques à l'état humide.

La compléxité de la contraction du tissu dépend non seulement de nombreux facteurs, mais aussi du fait qu'elle, peut être permanente ou elle peut se manifester une seule fois. La contraction qui se manifeste une seule fois est la contraction qui a lieu principalement au premier mouillage ou lavage. D'habitude elle disparaît après quelques lavages successifs; si l'action des tensions a été enlevée, la contraction du tissu peut aussi prendre un caractère permanent. Cela veut diré que le tissu se contracte avec une certaine valeur après chaque lavage ou autre processus à l'état, humide, même quand les tensions ont été éliminées.

La contraction permanente d'un tissu dépend de la capacité de feutrage des fibres. Une grande capacité de feutrage et donc une capacité de contraction permanente est présentée par les fils dont les fibres indépendantes effectuent une migration sous l'influence des forces qui agissent mécaniquement à l'état humide et ainsi elles s'enchevêtrent. Cette caractéristique spécifique aux tissus réalisés en fils de laine est mise au compte de la dépendance du coefficient de frottement des fibres de laine, du sens dans lequel le frottement a lieu. On a observé que d'autres fibres aussi, comme par exemple celles de fibranne, manifestent une capacité de reutrage. Cela pourrait être attribué à la diminution du module d'élasticité des fibres de fibranne à l'état numide.

À part les actions déjà citées, il existe encore une contraction du tissu causée par l'allongement excessif des fibres pendant le processus technologique. La contraction des tissus en fibres syntétiques, comme par exemple les fibres de polyester,

ne peut pas être expliquée ni par le gonflement des fibres, ni par la capacité de feutrage, parce que ces fibres ne se gonflent pas du tont dans l'eau et ne présentent aucune capacité de feutrage.

Pourtant, les tissu en ces fibres se contractent aussi.

Ce phénomène peut être expliqué seulement par l'allongement excessif du tissu dû aux tensions exécutées au tissage et ennoblissement, particulièrement pendant les processus technologiques humides. On peut constater que les tissus excessivement allongés présentent par comparaison une capacité plus grande de contraction. Ce genre de contraction est très visible aux fibres dont le module d'élasticité diminue beaucoup à l'état humide (exemple: les fibres de rayonne).

Un allongement excessif des fibres pendant la filature a comme conséquence une plus grande contraction du tissu.

Pendant que pour les tissus en fibres de rayonne les trois genres de contractions apparaissent simultanément, à savoir la contraction par le gonflement des fibres, par le feutrage et l'allongement excessif pendant la filature, pour d'autres fibres, seulement un ou deux genres de contractions apparaissent.

Un facteur important qui influence sensiblement les modifications dimensionnelles du tissu est la tension et la dé-tension qui agissent pendant la filature, le tissage, y compris la préparation de la chaîne et de la trame, jusqu'à l'ennoblissement du tissu. Surtout à la dernière étape du processus de fabrication, le tissu se trouve sous l'influence de grandes forces d'allongement, specialemént à l'état humide. Cela peut mener à la situation où le tissu parde cet allongement même au cours du séchage.

3. Aspects experimentaux. Au cours des expérimentations le but a été de mettre en évidence la relation entre la tension du tissu, dans la direction de la chaîne et de la trame (à l'état humide et sec) et les modifications dimensionnelles correspondant à deux systèmes d'armure, à savoir:

– tissu écru, armure diagonale de fils Nm 36/38 à composition fibreuse 55% fibranne et 45% fibres en polyester;

– tissu écru armure toile en fils du même numéro métrique et de la même composition fibreuse que pour le tissu cité ci-dessus.

Les tissus ont été arrosés pendant 20 minutes à 40°C dans un bain contenet un agent tensio-actif d'humidification (Aldetal N lg/l).

Après l'arrosage, les tissus ont été exprimés sur le foulard et tensionnés tant après l'exprimage qu'après le séchage.

La tension appliquée a eu des valeurs entre 2 et 11 kgf/10 cm (allongement 2...5%). Les valeurs des modifications dimensionnelles sont présentées graphiquement dans les figures 1,...,4.

De l'aspect des relations présentées graphiquement on voit que les modifications dimensionnelles dues à la tension dépendent de la structure du tissu. La comparaison de cette relation entre l'armure diagonale et l'armure toile montre que les modifications dimensionnelles dans la direction de la chaîne sous l'influence de l'augmentation de la tension, sur des tissus écrus secs ne diffèrent pas trop (Figs.1,...,4). La modification dimensionnelle en largeur s'est manifestée différemment. On peut observer que la perte dans la direction de la trame, tant pour l'armure toile que pour l'armure diagonale, est plus grande que l'augmentation dans la direction de la trame (Figs.1,...,4).

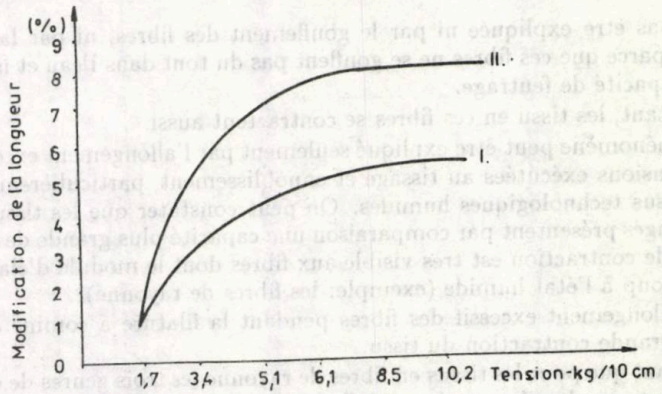

Fig. 1.– Modification dimensionelle dans la direction de longueur d'un tissu à armure toile sous l'action des tensions. I – humide; II – au séchage.

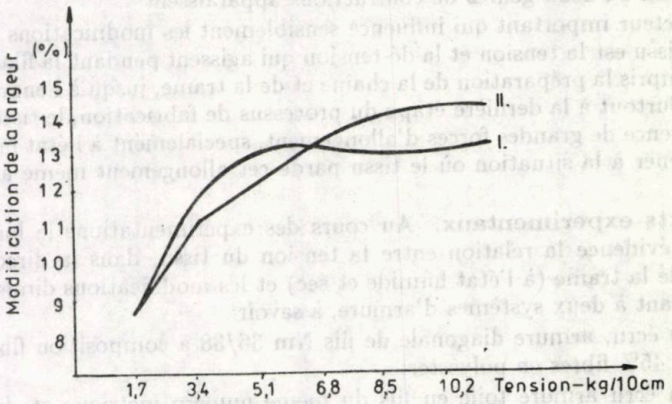

Fig. 2.– Modification dimensionnelle en largeur d'un tissu à armure toile sous l'action des tensions. I – humide; II – au séchage.

En comparant les valeurs absolus on peut constater que pour les structures de tissus examinés, elles ne diffèrent pas trop des autres quand la tension agit sur le tissu à l'état sec.

L'influence de la structure des tissus sur les modifications dimensionnelles sous l'action de la tension, devient visible au cycle humidification-séchage (Figs.1,...,4).

Au cours du cycle humidification-séchage premièrement il se passa une détension du tissu.

Une comparaison des valeurs absolues des modifications dimensionnelles des tissus examinés, armure toile et diagonale, montre que la même tension agit différemment sur les modifications dimensionnelles du tissu.

L'aspect graphique des relations nous conduit à la conclusion que les valeurs des modifications dimensionnelles n'augmentent plus d'une manière significative au-delà d'un certain niveau des valeurs de la tension.

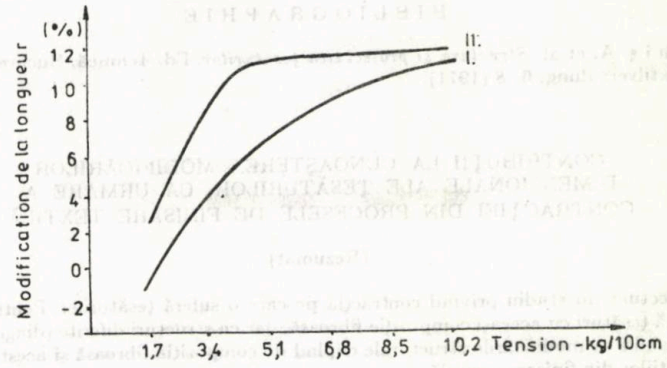

Fig. 3.– Modification dimensionnelle en longueur d'un tissu à armure diagonale sous l'action des tensions. I – humide; II – au séchage.

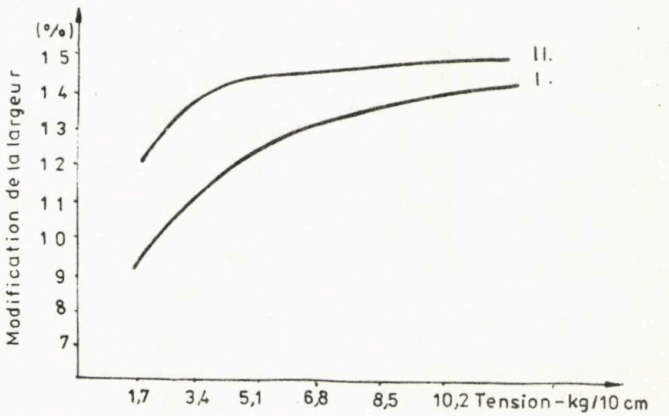

Fig. 4.– Modification dimensionnelle en largeur d'un tissu à armure diagonale sous l'action des tensions. I – humide; II – au séchage.

Les modifications dimensionnelles produites par la tension à l'humidification sont plus intensifiées par les tensions au cours du séchage.

Par conséquent, les tensions plus réuites dans les processus d'apprêt mouillé et sec peuvent contribuer à la diminution de la contraction des tissus ennoblis.

4. Conclusions. La réduction de toutes les forces d'allomgement pendant l'apprêt du tissu est la condition préalable pour une contraction réduite. Même si pendant le processus d'apprêt l'humidification est intense on n'optient pas un état d'équilibre de la structure du tissu parce que dans toutes les étapes du processus d'apprêt, surtout dans l'apprêt mouillé, d'importantes forces de tension agissent.

Même si par l'apprêt on peut réduire les contractions du tissu il n'est pas possible, pour le moment, une élimination complète de cet effet.

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CONTRIBUŢII LA CUNOAŞTEREA MODIFICĂRILOR DIMENSIONALE ALE ŢESĂTURILOR, CA URMARE A CONTRACŢIEI DIN PROCESELE DE FINISARE TEXTILĂ

(Rezumat)

S-a efectuat un studiu privind contracţia pe care o suferă ţesăturile. Pentru acesta s-au utilizat două ţesături cu aceeaşi compoziţie fibroasă, dar cu structuri diferite (diagonal şi pânză).

S-a stabilit că modificările structurale depind de compoziţia fibroasă şi acestea se reduc în urma operaţiilor din finisarea textilă.

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TEXTILE. PIELĂRIE

MÉTHODES DE CARACTÉRISATION DES PRODUITS ANTI-STATIQUES DANS LES FILATURES DE LAINE PEIGNÉE

PAR
VALERIA NISTOR et MARIN DINU

1. Introduction. Pour la réception des produits anti-statiques dans les fabriques textiles on utilise quelques méthodes de vérification qualitative comme: l'aspect de la solution 1%, le pH de la solution 1%, le contenu en matière sèche, etc. Les résultats de ces analyses ne réussissent pas à mettre en évidence l'efficacité des produits du point de vue anti-électrostatique, les seules données qui existent pour le technologue sont les informations fournies par le producteur dans les prospectus des produits respectifs, qui eux aussi sont assez généraux. La pratique industrielle a prouvé que pour une caractérisation complète des produits antistatiques, à part les données relatives au comportement des fibres traitées anti-statiquement sur les machines de la filature, il est nécessaire de faire d'autres déterminations physiques comme: la vérification de la charge électrostatique que ces produits assurent, le mesurage de la conductibilité électrique, le mesurage du coefficient de frottement statique et dynamique et la verification de comportaement dans le processus de frottement „fibre-métal" à l'occasion du soi-disant essai de débourrure.

2. Partie applicative

2.1. Pour le mesurage de la charge électrostatique des matières textiles on a construit les dernières années plusieurs appareils. On a enregistré de très bons résultats avec le statomètre Haose aux mesurage à l'échelle industrielle des matières qui se déplacent continuellement, avec une précion adaptée aux conditions rencontrées dans la pratique. Les résultats des mesurages de la charge électrostique s'expriment en V/m ou V/cm, en même temps on indique la polarité.

La charge électrostatique dépend de l'intensité du frottement, de la nature des matiéres textiles, de la vitesse avec laquelle se déplacent les matières textiles et d'autres facteurs incontrôlables.

Conformément aux données de la littérature de spécialité, les produits antistatisés qui se chargent à une valeur au-dessous, de 200 V/cm ne présentent pas de difficultés dans l'usinage à cause de la charge électrostatique [1].

Il est très possible que des difficultés apparaissent et la charge déplasse 1000 V/cm. Une méthode rapide et simple de déterminer les charges electrostatiques peut être la capacité d'attraction de la cendre.

Tout ce qu'on a affirmé ci-dessus a été confirmé dans le processus de filage d'un mélange de 60% fibre de polyester et 40% fibranne, avivé dans des condi-

tions industrielles, ayant comme but la charge électrostatique des fibres sur le flux technologique jusqu'à le préparation de la filature (Tableau 1).

Tableau 1

La variante de la charge électrostatique des fibres avivées pendant l'usinage dans la filature de laine peignée

No. crt.	Phase technologique	Charge électrostatique, V/m	Capacité d'être usiné
1.	Défeutrage	100-200	bonne
2.	Laminage après peignage	200-300	bonne
3.	Mélange	500 (la charge a haussé parce qu'au cours des opérations le recouvrement en anti-statisant diminue)	bonne
4.	La préparation de la filature	300-400	bonne

Il convient de rappeler que la charge électrostatique est influencée par l'humidité relative du microclimat des salles d'usihage des matiéres textiles.

2.2. Bien que les mesurages de résistance ne reflètent pas d'une manière appropriée les propriétés électrostatiques des fibres, ils sont nécessaires pour les études menées dans le domaine de la protection anti-statique. On mesure la résistance électrique de volume et la résistance électrique de surface. La résistance électrique de volume est déterminée en mesurant la densité de courant électrique.

Plus importante pour l'appréciation des effets des produits anti-statiques est la résistance électrique de surface parce que presque dans la totalité des cas, la charge électrostatique produite par frottement ou par contact se décharge sur la surface [2].

La résistance electrique de surface est mesurée de la même maniére que la résistance de volume.

Conformément à des résultats pratiques, les matiéres textiles ayant une résistance superficielle de $10^{16}\Omega$, se chargent électrostatiquement extrêmement fort tandis qu'à une résistance de $10^{18}\Omega$, le tissu ne se charge pas électrostatiquement.

Géneralement, une matiéres avec une résistance superficielle de $10^{10}\Omega$ est considérée anti-statisée [3].

A l'humidité reletive au-dessous de 30% l'augmentation de la résistance est évidemment très rapide et la charge avec électricité statique a l'effet le plus nuisible.

2.3. Pour le caractérisation des produits anti-statiques il est nécessaire aussi de mesurer la conductibilité électrique de la matiére antistatisée et non-antistatisée.

On a constaté pratiquement que l'usinage ne sera pas troublé par l'électricité statique qui se forme entre les fibres dont la conductibilité électrique a des valeurs d'environ $2.10^{-10}\Omega$.

Pour une conductibilité électrique au-dessous de $2.10^{-10}\Omega$ on peut obtenir de bons résultats dans l'usinage avec les produits anti-statiques utilisés.

La conductibilité électrique est mesurée avec l'appareil „Static-Woltmeter" produit par la firme Rotschild de Zürich.

Il y a une depéndance entre les propriétés anti-statiques des produits et la conductibilité électrolitique, (Fig.1 et Tableau 2) fait signalé dans la littérature de

Tableau 2

La dépandance entre la charge électrostatique et la conductibilité électrique[4]

No.	Substance pour anti-statisation	Conductibilité électrique, mA	Capacité d'électrisation des fils, V	
			Fil poilu Nm=54	Fil lisse Nm=15,6
1.	Novvol	10	750	2100
2.	Préparé K-160	17	600	1500
3.	Composition 13	30	400	1150
4.	Substance d'antistation 1	83	55	225
5.	Substance d'antistation 3	90	5	125
6.	Préparé BV	60	350	1050

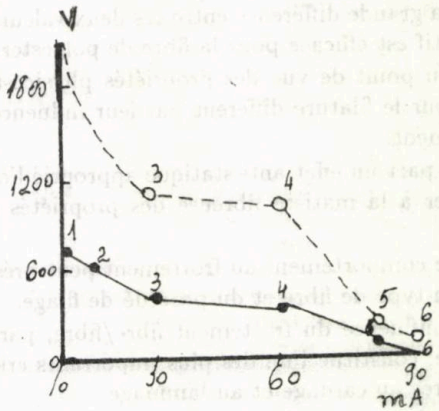

Fig. 1.– Dépendance de la charge électrostatique de la fibre de la conductibilité électrique.

spécialité [4].

Tant dans le Tableau 2 que dans la Fig.1 on présente la dépendance dont on a parté ci-dessus pour une fibre de polyamide avivée avec plusieurs produits fabriqués dans le laboratoire dans le but d'étudier ce phénomène.

2.4. Le temps, en secondes, pendant lequel la charge électrostatique s'élimine jusqu'à la moitié de sa valeur initiale, appelé période de demi-vie, nous donne une information précieuse sur la qualité antistatique de produit.

Les caractéristiques, anti-statiques des produits fonction de la période de demi-vie et de la résistance spécifique d'ecoulement sur la surface sont présentées dans le Tableau 3.

Tableau 3

Les caractéristiques anti-statiques des produits fonction de la période de demi-vie et de la résistance spécifique

Période de demi-vie, en secondes	Résistance spécifique d'éconlement sur la surface, en Ω	Caractéristiques anti-statiques
0,5	10^{10}	très bonnes
0,5 – 2	10^{12}	bonnes
2 – 10	10^{14}	satisfaisantes
10 – 100	10^{15}	non-satisfaisantes
100	10^{16}	zéro

Avec les mêmes appareils avec lesquels on determine la charge électrostatique on peut mesurer aussi la période de demi-vie.

Pour la vérification industrielle de l'inportance de ce paramétre des substances d'anti-statisation on a effectué cinq déterminations sur des éprouvettes de fibres de polyester teintes et avivées et sur des fibres qui n'ont pas été teintes et avivées: la conclusion a été que pour les fibres avivées la période de demi-vie de la charge électrostatique se situait à des valeurs comprises entre 1,5...1,6 sec., tandis que pour celles non-avivées la valeur était de 25,6 sec.

Dans le cas des fibres de laine avivées du même produit, la période de demi-vie a été de 70 sec. pour fibres non-avivées et entre 18 et 25 sec. pour fibres avivées.

La grande différence entre ces deux valeurs peut être due au fait que le produit respectif est efficace pour la fibre de polyester et moins efficace pour la laine.

2.5. Du point de vue des propriétés physico-technologiques, les produits auxiliares, pour le filature diffèrent par leur influence sur le comportement des fibres au frottement.

A part un effet anti-statique approprié l'auxiliaire chimique de la filature doit conférer à la matière fibreuse des propriétés optimales de frottement en vue du filage.

Le comportement au frottement peut présenter beaucoup de différences fonction du type de fibre et du procédé de filage.

L'influence du frottement fibre/fibre, par l'intermédiaire de l'auxiliaire pour filature, constitue l'un des plus importants critères pour évaluer le comportement des fibres au cardage et au laminage.

Le frottement des fibres doit être considéré sous deux aspects:

- frottement statique fibre/fibre (adhérence);
- frottement dinamique fibre/fibre (glissement).

A l'évolution du comportement au laminage des fibres courtes (fibres coupées) la valeur de l'adhérence entre les fibres doit être le critère principal: plus la longueur de la fibre est petite, plus la finesse est grande et plus le matissage est réduit, plus l'adhérence offerte par le produit auxiliaire doit être grande pour obtenir une fiabilité optimale. Le diagramme charge/élongation (Fig.2) présente dans le point *A* la capacité d'adhérence maximale qui peut être aussi exprimée par la valeur de la longneur d'adhérence.

Dans le diagramme de fiction (Fig.3) on retrouverales avivages (représentés par des points) qui conféints) qui confèrent à la matière fibreuse une adhérence accrue, dans la partie supérieure, et les avivages qui confèrent une adhérence réduite, dans la partie inférieure de la figure.

Le diagramme représente dans une forme schématique les valeurs des coefficients d'adhérence et de glissement possibles à réaliser avec les produits respectifs.

Plus le produit se trouve vers la gauche plus il determine un glissement plus grand; plus il se trouve plus haut, plus l'adhérence est grande.

La détermination des coefficients de frottement statique et dynamique des filaments traités avec les auxiliaires respectifs est effectées en mesurant le frottement

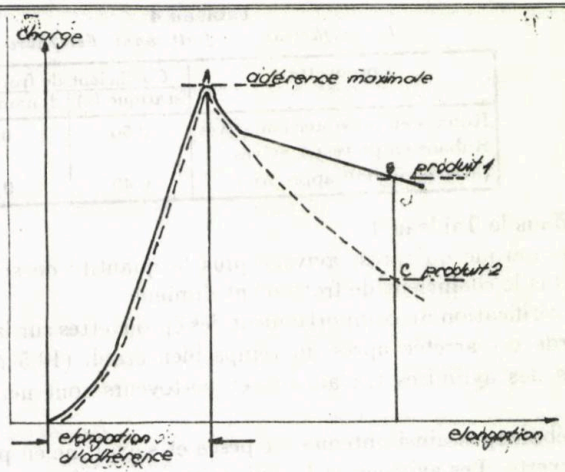

Fig. 2.– Diagramme charge/élongation pour deux produits d'anti-statisation.

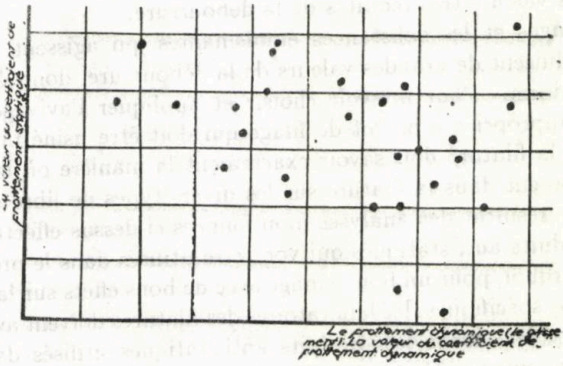

Fig. 3

sur un appareil spécial (l'appareil F-Meter Winder R 1083 de la firme Rothschild de Suisse).

La frottement dynamique fibre/fibre (le glissement) est représenté par la partie descendente du diagramme-élongation (Fig.2).

Les avivages qui confèrent à la matière fibreuse un frottement dynamique élevé, à savoir les produits de la partie droite du diagramme de friction, auront une allure plus aplatie (produit *1*), et les avivages qui confèrent un frotemment dynamique réduit dans la partie gauche du diagramma de friction auront une allure de descente plus grande (produit *2*).

Fonction de l'allure de la courbe charge-élongation, à savoir fonction de l'adhérence maximale et fonction de la branche relative au comportement au laminage des avivages et anti-statisants on utilisera le produit respectif.

Pour mettre en evidence l'influence de la substance d'avivage sur le coefficient de frottement des fibres en polyester on a fait des mesurages du coefficient de frottement fibre/fibre tant statiquement que dynamiquement et les résultats sont

Tableau 4
Le coefficient de frottemant fibre/fibre

Eprouvette	Coefficient de frottement	
	statique (s)	dynamique (d)
Rubans en polyester nonavivés	0,50	0,41
Rubans en polyester avivés (avec le produit approprié)	0,40	0,23

montrés dans le Tableau 4.

On remarque qu'après, avivage plus la quantité de substance d'avivage est grande, plus le coefficient de frottement diminue.

À la vérification du comporttement des éprouvettes sur la carde d'échantillonage, la carde est arrêtée après un temps bien établi (10,5 minutes) et après, les garnitures des aylindres travailleurs et nettoyeurs sont nettoyées avec un peine manuel.

La débourrure ainsi obtenue est pesée et s'exprime en pourcentages du poids de l'éprouvette. Les avivagés et les substances émulsifiantes à action de glissement mèment à des valeurs très réduites de la débourrure.

Les avivages et les substances émulsifiantes qui agissent d'une maniére adhérente produisent de grandes valeurs de la débourrure, donc ils sont mauvais.

3. Conclusions. Pour pouvoir choisir et appliquer l'avivage et la substance émulsifiante appropriés à un lot de filage qui doit être usiné industriellement, le spécialiste de la filature doit savoir exactement la manière où les divers produits auxiliaires agissent dans la filature sur les divers types de fibre et cette chose est facilitée par le résultat des analyses montionnées ci-dessus effectuées au cöurs des essais des produits anti-statiques qui vont être utilisés dans le processus de filage.

C'est pourquoi, pour un bon usinage avec de bons effets sur la qualité et sur les consommations spécifiques, les laboratoires des filatures doivent avoir l'appareillage nécessaire pour les essais des produits anti-statiques utilisés dans les processus technologiques conformément aux méthodes présentées dans cet article.

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METODE DE CARACTERIZARE A PRODUSELOR DE ANTISTATIZARE, ÎN FILATURILE DE LÂNĂ PIEPTĂNATĂ

(Rezumat)

Pentru o caracterizare completă a produselor de antistatizare folosite în filaturile de lână pieptănată, pe lângă metodele indicate de normele calitative de recepţie ale acestora şi a datelor experimentale, se mai impune executarea unor determinări fizice semnalate în literatura de specialitate (încărcarea electrostatică, rezistenţa electrică superficială, conductibilitatea electrică, timpul de înjumătăţire a încărcării electrostatice, coeficienţii de frecare statici şi dinamici etc.) ce ar putea garanta eficacitatea antistatizanţilor în vederea unei bune prelucrări a materialelor textile.

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DECLARATIVE SEMANTICS FOR DISJUNCTIVE LOGIC PROGRAMS

BY

VALERIA SLABU and COSTICĂ CAZACU

1. Introduction. For disjunctive logic programs there are two definitions for semantics: declarative semantics and procedural semantics. They are a simple and natural extension [1] of the semantics for H o r n programs developed by van E m d e n, K o w a l s k i and A p t.

Jack minker and two of his students, Arcot R a j a s e k a r and Jorge L o b o, proposed the first theoretical developments in the disjunctive logic programming and Rodney T o p o r stated the terminology of disjunctive database and disjunctive logic programs.

A procedural semantics provides an implementation-independent proof procedure for deriving inferences from disjunctive logic programs and it is based on proof theory.

Declarative semantics are defined using some interpretation. Two definitions are for declarative semantics: model-theoretic semantics and fixpoint semantics. Model-theoretic semantics specify a declarative semantics based on models which capture the logical consequence of programs. Fixpoint semantics specify a declarative semantics based on closure operator T_p which achieve a least fixpoint which captures the intended meaning of derivability of disjunctive programs. The equivalence of the fixpoint semantics with the model-theoretic semantics is based on fixpoint theory.

Both of these declarative semantics deal with positive information. Theories of negation define the negative information that can be assumed by default from disjunctive logic programs and it is based on some rule of negation. We present the theoretical developments of theories of negation in the follow paper.

2. Preliminaries. All definitions in what follows are relative to a fixed first-order alphabet. By convention, letters from the end of the alphabet will denote variables and letters from the beginning of the alphabet or strings of letters will denote constants.

A clause disjunctive is a construction of the form head←body, where the head is a disjunction of literals and the body is a conjunction of literals. We will denote the clause

$$\forall y_1 ... y_k (A_1 \vee ... \vee A_n \longleftarrow B_1 \wedge ... \wedge B_r),$$

where $A_1, ..., A_k$ are atoms, $B_1, ..., B_r$ are literals and $y_1, ..., y_k$ are all variables occuring in these, by $A_1, ..., A_n \longleftarrow B_1, ..., B_r$, $n \geq 1$, $r \geq 0$. If $n = 1$, then the clause is called a Horn clause or a program clause.

An assertion (a positive) clause is a program clause that has no body. A goal clause is of the from $\leftarrow B_1, ..., B_m$, $m \geq 0$, where the terms $B_1, ..., B_m$ is a conjunction of atoms.

A H o r n program is a finite set of program clause.

A disjunctive logic program is a finite set of disjunctive clause.

A substitution θ is a any countably infinite set of the terms $\theta = (t_0, t_1, ...)$. We also use the following alternative notation for substitution: $(V_{j_1}/s_1, V_{j_2}/s_2, ..., V_{j_n}/s_n)$, where $V_{j_1}, ..., V_{j_n}$ are the distinct variables and $s_1, ..., s_n$ are the terms. In the such situations will understand the substitution in that $t_{jk} = s_k$ for $k = 1, 2, ..., n$ and $t_j = V_j$ if $j \neq j_1, j_2, ..., j_n$.

By a ground instance $C\theta$ of a disjunctive clause, we mean that there is a substitution θ for variables in C such that $C\theta$ is ground (that is, not containg variables).

The H e r b r a n d universe U_P of a logic program is the set of all ground terms which can be formed with the constants and functions symbols that apear in P (if no constants appear in P, then an arbitrary constant is used in U_P).

The H e r b r a n d base B_P of a logic program is the set of all ground atoms which can be formed by using predicates from P with ground terms from the H e r b r a n d universe U_P as arguments.

A H e r b r a n d interpretation I for P is a subset of the Herbrand base of P, in which all atoms are assumed to be true, while those not in I are assumed to be false.

A model of a logic program P is a H e r b r a n d interpretation of P that makes all clause in P true. A model M of logic program P is the least model of P, if it contains less positive atoms than any other model M' of P.

The extended H e r b r a n d base EB_P of a disjunctive logic program P is the set of all positive clauses which can be formed using distinct ground atoms for B_P. Obviously, $B_P \subseteq EB_P$.

The extended H e r b r a n d base of size $-k$ positive clause $EB_k(P)$ of the disjunctive logic program P is the set all positive clauses formed by taking the disjunction of k distinct ground atoms from the Herbrand base of the program P. Obviously, $EB_P = EB_\infty(P)$ and $EB_1(P) = B_P$.

A state of a disjunctive logic program P is a subset of $EB(P)$. Other information is given in [6].

3. Fixpoints. In logic programming a certain monotonic mapping associated with each program and hers fixpoint play a predominant role in the semantical discussions. The least fixpoint of mapping characterizes the positive information in a

logic program, the greatest fixpoint bears some relationship to negative information in a logic program. For the disjunctive logic program, we define a immediate consequence operator (fixpoint operator) T_P over the extended Herbrand base of a program P. The least fixpoint of T_P is the set of all positive ground clauses derivable from P.

First of all we review the basic results and definitions with the fixpoint theory. All details of fixpoint theory may be found in [3], [4].

3.1. Basic Definitions of Fixpoint Theory. Let S be a set with partial order. Then $a \in S$ is an upper bound of a subset X of S if $x \leq X$ for all $x \in X$. Similary, b is a lower bound of X if $b \leq x$, for all $x \in X$. Then $a \in S$ is the least upper bound of a subset X of S if a is an upper bound of X and, for all upper bounds a' of X, we have $a \leq a'$.

Similary, b is a greatest lower bound of a subset X of S if b is a lower bound of X and, for all lower bound b' of X, we have $b' \leq b$.

If the least upper bound of X exists, it is unique, and is denoted by $\text{lub}(X)$.

Similary, if the greatest lower bound of X exists, it is unique, and is denoted by $\text{glb}(X)$.

A partially ordered set L is a complete lattice if $\text{lub}(X)$ and $\text{glb}(X)$ exist, for every subset X of L.

Definition 3.1.1. Let L be a complete lattice and $T : L \to L$ be a mapping. T is monotonic if $T(x) \leq T(y)$, whenever $x \leq y$. T is continuous is $T(\text{lub}(X)) = \text{lub}(T(X))$, for every directed subset$X$ of L.

A subset X of L is directed if every finite subset of X has an upper bound in X.

Definition 3.1.2. Let L be a complete lattice and $T : L \to L$ be a mapping. $a \in L$ is the least fixpoint of T if a is a fixpoint (that is, $T(a) = a$) and for all fixpoint b of T, $a \leq b$. Similary, we define greatest fixpoint.

Proposition 3.1.1. Let L be a complete lattice and $T : L \to L$ be a monotonic mapping. Then T has a least fixpoint, $lfp(T)$, and a greatest fixpoint, $gfp(T)$.

The proof is in [3].

We will recall also the definition of the ordinal power of T.

Definition 3.1.3. Let L be a complete lattice and $T : L \to L$ be a monotonic mapping. Then we define:

$T \uparrow 0 = \bot$ (the bottom element $glb(L)$ of the complete lattice L);

$T \uparrow \alpha = T\ (T \uparrow (\alpha - 1))$ if α is a succesor ordinal;

$T \uparrow \alpha = lub(T \uparrow \beta : \beta < \alpha)$ if α is a limit ordinal;

$T \downarrow 0 = \top$ (the top element $\text{lfp}(L)$ of the complete lattice L);

$T \downarrow \alpha = T\ (T \downarrow (\alpha - 1))$ if α is a succesor ordinal;

$T \downarrow \alpha = glb(T \downarrow \beta : \beta < \alpha)$ if α is a limit ordinal.

The least α such that $T \uparrow \alpha = \text{lfp}(T)$ is called the closure ordinal of T.

The next proposition is a characterization of $\text{lfp}(T)$ under stronger assumption that T is continuous.

Proposition 3.1.2. Let T be a complete lattice and $T : L \to L$ be continuous. Then $\text{lfp}(T) = T \uparrow \omega$.

3.2. Declarative Semantics for Definite Horn Programs. The first theoretical developments were by Van E m d e n and K o w a l s k i in which they detailed declarative and procedural semantics of H o r n programs as a programming language.

They define a immediate consequence operator (called a fixpoint operator T_P or a closure operator T_P) on the set 2^{B_P} of the H e r b r a n d base of a H o r n program P. The power set 2^{B_P} of the H e r b r a n d base of a H o r n program P is a complete lattice under set inclusion.

The operator T_P maps a H e r b r a n d interpretation I to a H e r b r a n d interpretation $T_P(I)$ of a program P, such as:

$T_P(I) = \{A \in B_P : A \leftarrow B_1, ..., B_m,\ m \geq 0$, is a ground instance of a program clause in P, and $\{B_1, ..., B_m\} \subseteq I\}$.

The operator T_P is monotonic for H o r n programs with respect to set inclusion, the sequence $T_P^n(\phi)$, where n runs through the natural numbers (i.e. the finite ordinals) is nondecreasing. The limit of the sequence is its union, which is the least fixpoint of T_P.

$$T_P \uparrow 0 = T_P(\phi) = \{A \in B_P : A \longleftarrow \in P\};$$
$$T_P(n+1) = T_P(T \uparrow n) = T_P \uparrow n \cup \{A \in B_P : A \longleftarrow B_1, ..., B_m,$$
$$m \geq 0, \text{ is a ground instance of a program clause in } P, \text{ and}$$
$$\{B_1, ..., B_m\} \subseteq T_P \uparrow n\};$$

and $T_P \uparrow \omega = \bigcup_{n=0}^{\infty} T_P \uparrow n$.

Thus, $T_P \uparrow \omega$ is the least fixpoint of T_P.

Van E m d e n and K o w a l s k i have shown that the least fixpoint define the intended meaning of a H o r n program in the sense that an atom is in I if and only if it is a logical consequence of the program.

Thus, the success set of a definite H o r n program P which is the least Herbrand model of a definite H o r n program M_P is the least fixpoints of T_P and it is unique. This major result of the H o r n theory provides a fixpoint characterization of the least H e r b r a n d model of a definite H o r n program:

$$\begin{aligned} M_P &= \{A \in B_P : \ A \text{ is a logical consequence of } P\} \\ &= \text{glb}\{I : \ I \text{ is a Herbrand model for } P\} \\ &= \text{glb}\{I : \ T_P(I) \subseteq I\} \\ &= \text{lfp}(T_P) \\ &= T_P \uparrow \omega. \end{aligned}$$

SLD resolution is a procedural counterpart for the declarative semantics for definite H o r n programs.

3.3. Immediate Consequence Operator for Disjunctive Programs. The set of all states of a disjunctive logic program P is 2^{EB_P}, where EB_P is the extended H e r b r a n d base of P. 2^{EB_P} form a complete lattice under the partial order of set inclusion $\subseteq$. The bottom element (L) of the lattice is the null set, ϕ, and the top element ($\top$) of the lattice is EB_P.

Then we define the immediate consequence operator as follow.

Definition 3.3.1. Let P be a disjunctive logic program and S be a state of a program P. The immediat consequence operator (the closure operator, the fixpoint operator) for P is a mapping $T_P : 2^{EB_P} \to 2^{EB_P}$ that is defined such:

$$T_P(S) = \{C \in EB_P : C' \leftarrow B_1, ..., B_n \text{ is aground instance of a clause in } P \text{ and } B_1 \vee C_1, ..., B_n \vee C_n \text{ are in } S \text{ and } C'' = C' \vee C_1 \vee ... \vee C_n \text{ where } \forall i,\ 1 \leq i \leq n,\ C_i \text{ can be null, and } C \text{ is the smallest factor of } C''\}.$$

The smallest factor of a ground clause C' is defined as the clause C such that C contains only distinct atoms and $C \Longleftrightarrow C'$.

The fixpoint operator T_P is continuous and hence monotonic. For that we use the definition of a immediat consequence operator, the definition of continuous on a complete lattice and the next lemma:

Let X be a directed subset of 2^{EB_P}. Then, for a set of positive ground clauses $\{A_1, ..., A_n\}$, we have $\{A_1, ..., A_n\} \subseteq lub(X)$ iff $\{A_1, ..., A_n\} \subseteq I$ for some $I \in X$. Hence, it have a least fixpoint and $\text{lfp}(T_P) = T_P \uparrow \omega$.

The intended meaning of a disjunctive logic program is associated with terms derivability and provability. In the case of H e r b r a n d interpretations the notions of provability and derivability coincide.

Since any provable clause also has a subclause that is derivable from a program, we can restrict our intended meaning of a disjunctive logic program to derivable clauses without losing generality. That is, the intended semantics will achieve a state that contains all (and only) the clauses which are derivable from a program.

Definition 3.3.2. Let P be a disjunctive logic program. P derives a clause C ($P \underset{D}{\vdash} C$) if there is a finite sequence $C_1, C_2, ..., C_n$ of clauses such that C_i, with $i = \overline{1,n}$, is either a clause in P or a resolvent of clauses preceding C_i, and $C_n = C$.

Definition 3.3.3. Let P be a disjunctive logic program. A clause C is provable from P when it is a logical consequence of the program.

A derivable state of a program P is defined as follow:

Definition 3.3.4. A state of a program P in which all clauses are derivable from P is called a derivable state:

$$SDER(P) = \{S :\ S \text{ is a derivable state of } P\}.$$

The next theorem provides a characterization of the fixpoint semantics for a disjunctive logic program and it shows that the least fixpoint achieved using the fixpoint operator captures the intended meaning of derivability of the program.

Theorem 3.3.1. Let P be a disjunctive logic program.

The $\text{lfp}(T_P) = \{C \text{ is derivable from } P\}$. We show by induction on n, $n \geq 0$, that the sequence $T_P \uparrow n$ contains only clauses derivables from P, i.e., it contains

no clauses which are not derivable from P. Hence, $\mathrm{lfp}(T_P) = T_P \uparrow \omega$ contains only clauses derivable from P and $T_P \uparrow \omega$ is a state which contains the set of all ground clauses derivable from P. The proof is in [2].

4. Equivalence to Model Theory. We consider H e r b r a n d models for to provide the equivalence of the fixpoint semantics with the model semantics. There is a set of H e r b r a n d models which capture the intended meaning for a disjunctive logic program. The set of minimal models of P is denoted by $MM(P)$.

The model theoretic semantics for disjunctive program is based on minimala models.

Theorem 4.1. A positive clause C is a logical consequence of a program P if C is true in every minimal model of P. That is, $P \vdash C$ iff $\forall M \in MM(P)\ M \models C$.

The following result provides the equivalence of the fixpoint semantics with the model semantics.

Lemma 4.1. Given a program P, $\forall M \in MM(P)$, $M \models C$ iff $\mathrm{lfp}(T_P) \vdash C$.

In [2] an example is illustrated.

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SEMANTICI DECLARATIVE PENTRU PROGRAME LOGICE DISJUNCTIVE

(Rezumat)

Pentru programe logice disjunctive se prezintă două tipuri de semantici declarative: semantici de punct fix şi semantici bazate pe teoria modelelor. Echivalenţa lor se sprijină pe teoria de punct fix.

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RECENZII — BOOK REVIEWS

MALL G., *Total Quality Management, ISO 9000 und die betriebliche Arbeitsmedizin.* Expert Verlag, Renningen, 1994, 125 S., ISBN 3-8169-1175-7.

Seit mehr als zwanzing Jahren gibt es des Arbeitssicherheitsgesetz (ASIG), in dem die Aufgaben des Betriebsarztes geregelt werden. Dennoch gelang es bisher nur wenigen Unternehmen, den Betriebsarzt zum Funktionsträger im Betrieb zu machen. In den meisten Betrieben liegt somit wertvolle Manpower brach.

Im vorliegenden Buch wird zum ersten Mal ein Konzept vorgestellt, wie die betriebsärztliche Betreuung sinnvoll in den Betriebsalltag als Beitrag zur Verbesserung der Prozeßqualität eingebunden werden kann. Denn Fachleute sind sich einig, daß die Forderungen des klassischen Arbeitsschutzes in vielen Firmen ausreichend eingehalten werden. Wettbewerbsvorteile für die Firmen lassen sich daher nur noch erzielen, wenn es gelingt, die betriebsärztliche Betreuung über die traditionellen Inhalte hinaus weiterzuentwickeln. Wenn dies im Rahmen der gesetzlich vorgeschriebenen Einsatzzeit erfolgt, entstehen dem Betrieb keinerlei Zusatzkosten.

Im einzelnen geht es um die Aufgaben des Betriebsarztes im Rahmen der DIN ISO 9000. Es werden Ergänzungen zum Qualitätssicherungshandbuch und eine Verfahrensanweisung vorgestellt. Konkrete Konzepte beschäftigen sich mit Eignungsanfragen, Qualitätszirkeln, Arbeitszeitflexibilisierung, Ergonomie, Fehlzeiten, Alkohol, Betriebshygiene u.a. Diese Konzepte sind praxisnah und können in jedem Betrieb sofort umgesetzt werden.

Die Interessenten:

Das Buch ist unentbehrlich für alle Führungskräfte der Personalabteilung, der Qualitätssicherung, der Produktion und des betriebsärztlichen Dienstes.

DÖRFEL H.J., *Projektmanagement.* Expert Verlag, Renningen, 1995, 100 S., ISBN 3-8169-1225-7.

Das Buch soll denjenigen als Leitfaden und Arbeitsunterlage dienen, die eine Projektorganisation einzurichten und Projektaufgaben zu erledigen haben. Es steckt darüber hinaus den Rahmen ab, um im Sinne von DIN ISO 9000 ff. ein Qualitätssicherungssystem für Projektmanagement festzulegen. Ausgerichtet ist die Thematik auf die Abwicklung von Aufträgen im Anlagenbau und in der Bauindustrie. Die inhaltlichen Schwerpunkte liegen in den Teilthemen

- Strukturplanung,
- Ablauf- und Terminplanung,
- Überwachung, Berichtswesen, Fortschrittsanalyse,
- Steuerung und Planaktualisierung.

Speziell angesprochen werden Projektleiter, denen aufgezeigt wird, wie ein Projekt erfolgversprechend aufgeplant, überwacht und gesteuert werden muß, sowie das Projektcontrolling für dessen Tätigkeitsbereiche dieses Buch die Meßlatte vorgeben soll. Der Unternehmensführung wird dargestellt, wie Projektmanagement in die bestehende Organisation integriert und wie der Durchsetzungsprozeß hinsichtlich Verfahrensweise, Adaption der beteiligten Stellen und Personen sowie Akzeptanz der erforderlichen Hilfsmittel und Werkzeuge bestmöglich vollzogen werden kann.

BARKOWSKI D., *Erfolg auf dem Messestand.* Expert Verlag, Renningen, 1993, 86 S., ISBN 3-8169-0858-6.

Das Buch ist ein "Muss" für alle Standbesatzungen auf Messen. Es verdeutlicht die Unterschiede zwischen einer "normalen" Verkaufssituation und der besonderen Situation auf einer Messe, macht deutlich, welche Verhaltensweisen Messebesucher "abschrecken", und zeigt statt dessen ein angemessenes (sprachliches und nichtsprachliches) Verhaltensrepertoire auf.

Es wendet sich an alle Mitarbeiter, die ihr Unternehmen an einem Messestand vertreten und alle Weiterbildungsbeauftragte oder Marketingleiter, die ihr Personal auf den Messeeinsatz vorbereiten.

I n h a l t: Vorbereitung (Ziele setzen, Zielgruppen abklären, Besonderheiten/Vorteile der Firma definieren) – Das Verhalten am Messestand (Den Besucher abschreckendes Verhalten, Vor der Kontaktaufnahme, Analyse des Besuchers, Kontaktaufnahme, Messespezifische Bedarfsanalyse, Informieren und Präsentieren, Besondere Gesprächssituationen) – Sonstige Hinweise (Namensschilder, Gesprächskontrolle, Kleiderordnung, Essen, Trinken und Rauchen am Stand, Standleiter, Prospekte) – Nachbereitung.

SCHULTHEISS W., *LEAN-Management.* Expert Verlag, Renningen, 1995, 225 S., ISBN 3-8169-1176-5.

Das Buch befaßt sich umfassend mit dem modernen "schlanken" Management-Ansatz und gibt einen aktuellen Überblick über den Stand der Erkenntnisse aus Wiessenschaft und Praxis.

Es zeigt konkrete Ansätze zur Umsetzung in nahezu allen betrieblichen Bereichen auf, ist praxisbezogen, orientiert sich an der betrieblichen Realität und ist keine utopische Übertragung fernöstlicher Methoden und Ansätze auf unsere Verhältnisse. Dem Leser werden:

– die LEAN-Strategie und Grundsätze zur Gestaltung der Führungsarbeit,

– der konkrete operative Weg zur Umsetzung über eine Gestaltung der Strukturen, einer rationellen Gestaltung der Geschäftsprozesse und des kontinuierlichen Verbesserungsprozesses (KAIZEN) Verbesserungsprozesses (KAIZEN) aufgezeigt. Dabei kommt es zu einer ganzheitlichen (systemischen) Darstellung des LEAN-Management.

Das Buch wendet sich an Personen, die Handlungsbedarf zur Überwindung der Struktur- und Kostenkrise in ihren Unternehmen erkennen und sich dabei für rationelle und zukunftsweisende Unternehmensstrukturen und -prozesse interessieren, jedoch auch an diejenigen Personen, die Vorbehalte gegenüber LEAN-Management haben. Das Buch trägt zur Aufklärung und "Entmythifizierung" von LEAN-Management bei.

MŰSZAKI INFORMÁCIÓS ÉS KÖNYVTÁR
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